



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460


OPP OFFICIAL RECORD
HEALTH EFFECTS DIVISION
SCIENTIFIC DATA REVIEW
EPA SERIES 361


OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

MEMORANDUM

DATE: 27-FEB-2002

SUBJECT: PP#1F06235. Diflubenzuron (Dimilin®) on Peppers, Stone Fruits (Except Cherries), and Tree Nuts (and Pistachios). **Evaluation of Residue Data and Analytical Methods.** MRID#s 452522-06 thru -11. Chemical 108201. Barcode D277691. Case 293515. Submission S602900.

FROM: George F. Kramer, Ph.D., Chemist 
Registration Action Branch 1 (RAB 1)
Health Effects Division (HED) (7509C)

THRU: G. Jeffrey Herndon, Branch Senior Scientist 
RAB1/HED (7509C)

TO: Arnold Layne/Ann Sibold, PM team 3
Registration Division (RD) (7505C)

Uniroyal Chemical Company, Inc. has submitted a petition for the establishment of permanent tolerances for the combined residues of the insect growth regulator diflubenzuron and metabolites convertible to p-chloroaniline (PCA), expressed as diflubenzuron, in/on the following raw agricultural commodities:

Almond hulls	5.0 ppm
Peppers	1.0 ppm
Stonefruit (except cherries)	0.05 ppm
Tree nuts and pistachios	0.05 ppm

In addition, Uniroyal has proposed to increase the established tolerance on meat byproducts from 0.05 to 0.15 ppm in connection with the increase in the tolerance for rangeland grass from 3.0 ppm to 6.0 ppm (65 FR 47882, Aug. 4, 2000).

In conjunction with the subject tolerance petition, Uniroyal has applied for Section 3 registration of an 80% water-dispersible

granule (WDG) formulation (Dimilin® 80WG; EPA File Symbol No. 400-XXX), and for amended registration of a 2 lb/gal flowable concentrate (FIC) formulation (Dimilin® 2L; EPA Reg. No. 400-461), for foliar use on peppers, Stone fruits (except cherries), and tree nuts, including pistachios. Diflubenzuron is a List A reregistration chemical (Case No. 0144) currently registered for use on apples, citrus (orange, tangerine, and grapefruit), cotton, grass, mushrooms, pears, soybeans, rice, walnuts, and non-food/feed crops.

The attached contractor's document has been reviewed and revised to reflect current HED policy.

Executive Summary of Chemistry Deficiencies

- Revised labels.
- Revised Section F.
- A successful Petition Method Validation (PMV) of analytical enforcement methods for crops.

RECOMMENDATIONS

Provided Sections B and F are revised, HED concludes there are no residue chemistry data requirements that would preclude the establishment of a conditional registration and permanent tolerances for the combined residues of diflubenzuron and its metabolites 4-chlorophenylurea (CPU) and PCA in/on the following RACs:

Pepper	1.0 ppm
Fruit, stone, group, except cherries	0.07 ppm
Nut, tree, group	0.06 ppm
Almond, hulls	6.0 ppm
Pistachio	0.06 ppm
Cattle, Meat Byproducts	0.15 ppm
Goat, Meat Byproducts	0.15 ppm
Hog, Meat Byproducts	0.15 ppm
Horse, Meat Byproducts	0.15 ppm
Sheep, Meat Byproducts	0.15 ppm

A human-health risk assessment will be prepared as a separate document.

HED recommends that conversion of the conditional registration of Dimilin® to unconditional registration may be considered upon submission of the following data:

Chemistry

- ▶ Successful Agency PMV of analytical enforcement methods for PCA and CPU in crops.

Attachment 1- contractor review

cc: Kramer

RDI: G. Herndon (2/21/02), RAB1 Chemists (2/21/02)

G.F. Kramer:806T:CM#2:(703)305-5079:7509C:RAB1

Attachment 1

DIFLUBENZURON
PC Code 108201
(DP Barcode D277691)

PP#1F06235: Summary of Residue Chemistry Data
to Support Permanent Tolerances for Use of
Diflubenzuron
on Peppers, Stone fruits (Except Cherries), and
Tree Nuts (and Pistachios)

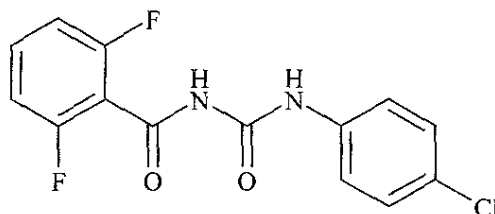
January 30, 2002

Contract No. 68-W-99-053

Submitted to:
U.S. Environmental Protection Agency
Arlington, VA

Submitted by:
Dynamac Corporation
20440 Century Boulevard, Suite 100
Germantown, MD 20874

DIFLUBENZURON



PP#1F06235: SUMMARY OF RESIDUE CHEMISTRY DATA TO SUPPORT
PERMANENT TOLERANCES FOR USE OF DIFLUBENZURON ON PEPPERS, STONE
FRUITS (EXCEPT CHERRIES), AND TREE NUTS (AND PISTACHIOS)

PC Code 108201; Case 293515

(DP BARCODE D277691)

INTRODUCTION

Uniroyal Chemical Company, Inc. has submitted a petition for the establishment of permanent tolerances for the combined residues of the insect growth regulator diflubenzuron and metabolites convertible to PCA, expressed as diflubenzuron, in/on the following RACs:

Almond hulls	5.0 ppm
Peppers	1.0 ppm
Stonefruit (except cherries)	0.05 ppm
Tree nuts and pistachios	0.05 ppm

In addition, Uniroyal has proposed to increase the established tolerance on meat byproducts from 0.05 to 0.15 ppm in connection with the increase in the tolerance for rangeland grass from 3.0 ppm to 6.0 ppm (65 FR 47882, Aug. 4, 2000).

In conjunction with the subject tolerance petition, Uniroyal has applied for Section 3 registration of an 80% WDG formulation (Dimilin® 80WG; EPA File Symbol No. 400-XXX), and for amended registration of a 2 lb/gal FlC formulation (Dimilin® 2L; EPA Reg. No. 400-461), for foliar use on peppers, Stone fruits (except cherries), and tree nuts, including pistachios. Diflubenzuron is a List A reregistration chemical (Case No. 0144) currently registered for use on apples, citrus (orange, tangerine, and grapefruit), cotton, grass, mushrooms, pears, soybeans, rice, walnuts, and non-food/feed crops.

Tolerances are currently established under 40 CFR §180.377(a)(1) for residues of diflubenzuron (N-[[4-chlorophenyl]

amino]carbonyl]-2,6-difluorobenzamide) in/on artichokes (6 ppm), cottonseed (0.2 ppm), grapefruit (0.5 ppm), mushrooms (0.2 ppm), orange (0.5 ppm), soybeans (0.05 ppm), soybean hulls (0.5 ppm), tangerine (0.5 ppm), walnuts (0.1 ppm), and livestock commodities (eggs, milk, fat, meat by-products, and meat; 0.05 ppm).

Tolerances are established under 40 CFR §180.377(a)(2) for residues of diflubenzuron and its metabolites CPU and PCA on rice grain (0.02 ppm), rice straw (0.8 ppm), and rangeland grass (6 ppm; 65 FR 47882, Aug. 4, 2000). Section 18 emergency exemption time-limited tolerances are established under 40 CFR §180.377(b) for residues of diflubenzuron and its metabolites, PCA and CPU, expressed as parent diflubenzuron, in/on pears (0.5 ppm; expiration date 3/31/01), and tolerances with regional registrations are established under 40 CFR §180.377(c) for residues of diflubenzuron in/on grass, pasture (1 ppm).

This memo provides a summary of the status of the diflubenzuron residue chemistry database as it supports the proposed uses. Detailed reviews providing more information about the following studies are available in separate memos (in the template DER format): crop field trial data for peppers (45252211.der.wpd & 45252211.de2.wpd), stone fruits (except cherries) (45252206.der.wpd & 45252208.de2.wpd), and tree nuts (4525209.der.wpd).

CONCLUSIONS/RECOMMENDATIONS

Provided Sections B and F are revised, HED concludes there are no residue chemistry data requirements that would preclude the establishment of a conditional registration and permanent tolerances for the combined residues of diflubenzuron and its metabolites CPU and PCA in/on the following RACs:

Pepper	1.0 ppm
Fruit, stone, group, except cherries	0.07 ppm
Nut, tree, group	0.06 ppm
Almond, hulls	6.0 ppm
Pistachio	0.06 ppm
Cattle, Meat Byproducts	0.15 ppm
Goat, Meat Byproducts	0.15 ppm
Hog, Meat Byproducts	0.15 ppm
Horse, Meat Byproducts	0.15 ppm
Sheep, Meat Byproducts	0.15 ppm

A human-health risk assessment will be prepared as a separate document.

HED recommends that conversion of the conditional registration of Dimilin® to unconditional registration may be considered upon submission of the following data:

Chemistry

- ▶ Successful Agency PMV of analytical enforcement methods for PCA and CPU in crops.

DATA SUMMARY

OPPTS 830 Series GLNs: Product Properties

Adequate product chemistry data have been submitted for the diflubenzuron TGAI (Product Chemistry Chapter of the Diflubenzuron Reregistration Eligibility Decision Document (RED) dated 3/15/95), except that additional data are required pertaining to preliminary analysis. Product-specific data (MRID 45252202) submitted for the end-use product Dimilin® 80WG (EPA File Symbol No. 400-XXX) are deferred to the Registration Division (RD). No additional product chemistry data concerning the diflubenzuron TGAI are required in support of this petition.

OPPTS GLN 860.1200: Proposed Uses

Uniroyal has submitted specimen labels for the 80% WDG formulation (Dimilin® 80WG; EPA File Symbol No. 400-XXX) and the 2 lb/gal FlC formulation (Dimilin® 2L; EPA Reg. No. 400-461). The 80% WDG and 2 lb/gal FlC formulations are proposed for foliar use on peppers, stone fruits (except cherries), and tree nuts, including pistachios. The petitioner has indicated that the 80% WDG formulation is identical to an 80% WDG formulation (Micromite® 80WG; EPA Reg. No. 400-487) that is currently registered for use on citrus in Florida only. The 2 lb/gal FlC formulation is currently registered for use on cotton, soybeans, rice, rangeland grass, and non-food/feed crops. The proposed use patterns are summarized below.

Peppers (bell and non-bell): The 80% WDG and 2 lb/gal FlC formulations are proposed for up to five foliar applications, at 7-day retreatment intervals (RTIs), to peppers at 0.0625-0.125 lb ai/A/application; a maximum seasonal rate of 0.625 lb ai/A/year is implied. Applications are to be made in a minimum of 30 gal/A of water using ground equipment. Adjuvants or emulsified vegetable or paraffin crop oil (1 pint to 2 quarts/A) may be added to the finished spray. A preharvest interval (PHI) of 7 days is specified.

Stone fruits (excluding cherries): The 80% WDG and 2 lb/gal FlC formulations are proposed for up to two foliar applications, with a 21-day retreatment interval, to stone fruits (excluding cherries) at 0.125-0.25 lb ai/A/application, for a maximum seasonal rate of 0.50 lb ai/A/year. Applications are not to be made after petal fall. Applications are to be made in a minimum of 50 gal/A for small trees (≤ 10 feet tall) or 100 gal/A for larger trees using ground equipment. Oil should be added to the finished spray when treating for peach twig borer. A PHI is not proposed for stone fruits because applications after petal fall are prohibited.

Tree nuts, including pistachios: The 80% WDG and 2 lb/gal FlC formulations are proposed for up to four (three for walnuts) foliar applications, at 21-day RTIs, to tree nuts (including almond, beech nut, Brazil nut, butternut, cashew, chestnut, chinquapin, filbert (hazelnut), hickory nut, macadamia nut (bush nut), pecan, walnut (black and English), and pistachios) at 0.125-0.25 lb ai/A/application, for a maximum seasonal rate of 1 lb ai/A/year. Applications are to be made in a minimum of 50 gal/A for small trees (≤ 10 feet tall) or 100 gal/A for larger trees using ground equipment. Narrow range oil may be added to the finished spray for dormant stage applications at up to 8 gal/A, and vegetable oil may be added to the finished spray for other applications at 1 quart/A. A PHI of 28 days is specified.

Both specimen labels include general label restrictions specifying that applications may not be made through any type of irrigation system and that ground applications are not to be made within 25 feet of bodies of water such as lakes, reservoirs, rivers, permanent streams, natural ponds, marshes, or estuaries. A 12-hour restricted entry interval is specified. Although the label for the 80% WDG formulation does not specify any rotational crop intervals, the label for the 2 lb/gal FlC formulation prohibits planting food or feed crops (other than those registered for use) within 1 month of application.

The proposed use directions on peppers, stone fruits (except cherries), and tree nuts (including pistachios) for the 80% WDG and 2 lb/gal FlC formulations are adequate to allow HED an assessment of whether the submitted residue data reflect the maximum residues likely to occur in peppers, stone fruits (except cherries), and tree nuts, including pistachios, with the exception of the use of the 2 lb/gal FlC formulation on peppers.

For registration purposes, the petitioner should submit a revised Section B reflecting the following changes. For peppers, because no oil was added to the application sprays in the field trials, the submitted data will not support the use of adjuvants or oil; therefore, the use directions for the addition of adjuvants or oil should be removed. In addition, no data reflecting

application of the 2 lb/gal FlC formulation to peppers were submitted. This use should thus be deleted from the 2 lb/gal FlC label. Also, if the petitioner wishes to maintain a 30-day plantback interval for peppers on diflubenzuron labels, new limited field trials should be conducted reflecting application of diflubenzuron at 0.625 lb ai/A; otherwise, a 12-month plantback interval should be established. For tree nuts, including pistachios, the petitioner should submit a revised Section B to reflect the application timing represented in the field trials. The 2 lb/gal FlC and 80% WDG labels should be amended to specify RTIs and/or growth stages at which individual applications are to be made. In the field trials, applications were made when trees were dormant to pre-bud swell (application 1), at bloom to petal fall (application 2), at flowers/leaves/immature nut formation (application 3) and at hull split (application 4). RTIs were ~21 days between applications 1 and 2; 72-83 days between applications 2 and 3 for almonds and 21-28 days for pecans; and 70-175 days between applications 3 and 4. The submitted data for tree nuts not support the addition of oil to the tank mix for any applications other than the initial dormant stage application; therefore, the directions for the addition of 1 quart/A of oil to other stage applications should be removed.

OPPTS GLN 860.1300: Nature of the Residue in Plants, Fungi and Livestock

The qualitative nature of the residue in plants, fungi and livestock is adequately understood based on data from citrus, mushroom, rice, and soybean, and ruminant and poultry metabolism studies. In the tolerance reassessment conducted for the Diflubenzuron RED (8/97) it was concluded that the tolerance for diflubenzuron should be expressed in terms of the combined residues of diflubenzuron and metabolites convertible to PCA. However, in consideration of the results of additional toxicity testing, the HED Metabolism Assessment Review Committee (MARC) has concluded (DP Barcode D272976, 5/31/01, G. Kramer) that the tolerance expression for diflubenzuron should include diflubenzuron, CPU and PCA.

OPPTS GLN 860.1340: Residue Analytical Method - Plants

Enforcement methodology is available or pending for the analysis of residues of diflubenzuron, CPU, and PCA in plant commodities. For determination of residues of diflubenzuron, Pesticide Analytical Method Volume II (PAM II), Method I is a GC/ECD method that determines diflubenzuron in plants by derivatization of the cleavage product, PCA. A GC/ECD method for residues of CPU (limit of quantitation (LOQ) of 0.001 ppm) and a GC/MS method for

residues of PCA (LOQ of 0.005 ppm) have been proposed for the enforcement of tolerances in connection with a rice petition (PP#8F4925; DP Barcode D240107, 6/23/98, G. Kramer; and DP Barcodes D253043, D253041, D244487, D251221, and D251609, 2/17/99, G. Kramer). The methods and ILVs have been sent to the ACL for PMV (PP#8F4925; DP Barcode D251484, 12/15/98, J. Rowell) on rice grain, straw, hulls, and bran. HED will withhold a final conclusion on the adequacy of these methods as analytical enforcement methods pending receipt of the PMV reports. However, because these methods are based on PAM Vol. II, Method II (a GC/ECD method that can separately determine residues of diflubenzuron, CPU, and PCA in eggs, milk, and livestock tissues), HED has no objections to conditional registration while the PMV of the methods for CPU and PCA in rice commodities is performed.

Samples of peppers, peaches, and plums were analyzed for residues of diflubenzuron using GC/ECD methods similar to PAM Vol. II, Method I, and samples of almond and pecan nutmeats and hulls were analyzed for residues of diflubenzuron using an HPLC/UV method. For residues of CPU, samples of peppers and peaches (from the 1997 field trials) were analyzed using GC/ECD methods identical or similar to the one submitted for the rice petition, and samples of peaches (from the 1998 field trials), plums, and almond and pecan nutmeats and hulls were analyzed using an HPLC/MS method. For residues of PCA, samples of peppers, peaches, plums, and almond and pecan nutmeats and hulls were analyzed using the GC/MS method submitted for the rice petition. Based on the method validation and concurrent method recovery data, these methods are adequate for data collection.

The validated method LOQs were 0.005-0.05 ppm for diflubenzuron, 0.005-0.01 ppm for CPU, and 0.005 ppm for PCA in peppers.

OPPTS GLN 860.1340: Analytical Methods - Livestock

Adequate methods are available for the analysis of diflubenzuron, CPU, and PCA in livestock commodities. PAM Vol. II, Method II is a GC/ECD method that can separately determine residues of diflubenzuron, CPU, and PCA in eggs, milk, and livestock tissues, each as derivatized PCA. PAM Vol. II, Method III is an HPLC/UV method that determines residues of diflubenzuron *per se* in eggs, milk, and livestock tissues.

OPPTS GLN 860.1360: Multiresidue Method

The FDA PESTDATA database dated 11/01 (PAM Vol. I, Appendix II) contains no information on diflubenzuron recovery using Multiresidue Methods, PAM, Vol. I Sections 302, 303, and 304.

However, the registrant has submitted Multiresidue testing data that the Agency has forwarded to the FDA (DP Barcode D194722, 9/17/93, L. Edwards). The PESTDATA database indicates that PCA is not recovered using Multiresidue Method Sections 302, 303, or 304, and that CPU is not recovered using Sections 303 and 304, but there is small recovery (<50%) of CPU using Section 302.

OPPTS GLN 860.1380: Storage Stability Data

Maximum storage intervals for field trial samples prior to analysis for diflubenzuron, CPU, and PCA, respectively, were 340, 357, and 347 days (<12 months) for peppers; 293, 407, and 351 days (~10, 14, and 12 months) for peaches; 200, 326, and 298 days (~7, 11, and 10 months) for plums; 151, 312, and 148 days (~5, 10.5, and 5 months) for almonds; and 92, 195, and 178 days (~3, 6.5, and 6 months) for pecans. Maximum storage intervals of plum RAC and prunes from the processing study prior to analysis of diflubenzuron, CPU, and PCA were 172 and 198 days (~6-7 months) for diflubenzuron in/on plums and prunes, respectively; 291 days (<10 months) for CPU in/on plums; and 263 and 262 days (<9 months) for PCA in/on plums and prunes, respectively.

In support of the pepper field trials, the petitioner conducted a concurrent freezer storage stability study (MRID 45252211), in which samples of homogenized bell peppers were spiked separately with diflubenzuron, CPU, and PCA at levels of 0.5, 0.1 and 0.1 ppm, respectively, and were stored frozen for 12 months. Refer to D277691, DER 860.1380 for a review of these data. The storage stability data indicate that residues of diflubenzuron per se were relatively stable in bell peppers stored frozen for up to 12 months. Residues of CPU declined ~20% following 3 months of frozen storage but did not decline further through the study. Residues of PCA in fortified bell pepper samples declined ~30% following 1 month of frozen storage, and continued to decline through the study; following 12 months of frozen storage residues had declined ~70%.

This freezer storage stability study is classified acceptable and satisfies the guideline requirement for a freezer storage stability study (Residue Chemistry Guidelines OPPTS 860.1380), and is sufficient to support the storage intervals and conditions of samples from the pepper field trial studies.

In support of the field trials for stone fruits and tree nuts, including pistachios, the petitioner referred to previously submitted storage stability data. The storage stability data that were summarized in the Residue Chemistry Chapter of the Diflubenzuron RED, dated 3/16/95, indicated that residues of diflubenzuron per se were stable under frozen storage conditions for up to 3 months in/on cottonseed, 16 months in/on oranges, and

12 months in/on mushrooms, milk, eggs, and beef and poultry tissues. Available data for apples, though inadequate, also suggested that residues of diflubenzuron *per se* were stable for up to 12 months in/on apples. Storage stability data for CPU indicated that residues were relatively stable for up to 6 months in/on frozen mushrooms. Storage stability data for CPU and PCA suggested that residues of these metabolites were stable in milk and liver stored frozen for up to 22 months; however, actual dates of sample fortification, extraction, and analysis were required to confirm the adequacy of these data. The RED required additional data depicting the stability of residues of diflubenzuron *per se* residues to support the storage intervals and conditions for residue samples used to support tolerances.

Additional storage stability data were submitted in conjunction with petitions for pears (PP#6E6167; D272978, 4/3/01, G. Kramer) and rice (PP#8F4925; DP Barcodes D253043, D253041, D244487, D251221, and D251609, 2/17/99, G. Kramer). These data indicate that residues of diflubenzuron *per se* were stable in/on pears for up to 2.5 months and in/on rice commodities (rice grain, straw, hulls, and bran) for up to 12 months; residues of CPU were relatively stable in/on rice commodities for up to 12 months, but decreased following 3 months of storage in/on pears; and residues of PCA decreased significantly following 1 month of storage in/on pears and rice commodities.

The available storage stability data are adequate support the storage intervals and conditions for residues of diflubenzuron in/on pepper, peach, plum, almond, pecan, and prune samples from the field trial and processing studies. Although the available storage stability data indicate that residues in field samples stored for >1 month and >3 months for CPU should be corrected for apparent decline during storage, correction for loss on storage would not significantly affect the results of the subject field trial studies because residues of CPU and PCA were either below the LOQs (<0.005-0.01 ppm; much lower than the LOQ of diflubenzuron of 0.05 ppm) or were detectable at levels 1-4 orders of magnitude lower than those of diflubenzuron.

OPPTS GLN 860.1500: Magnitude of the Residue - Plants

In support of the proposed tolerances and foliar use of diflubenzuron on peppers, stone fruits (except cherries), and tree nuts, including pistachios, Uniroyal has submitted the results from supervised crop field trials on almonds (MRID 45252209), peaches (MRIDs 45252206 and 45252207), pecans (MRID 45252210), bell and non-bell peppers (MRID 45252211), and plums (MRID 45252208); refer to D277691, DERs 860.1500 for review of these data. The submitted data are summarized below.

Peppers

Uniroyal has submitted the results from supervised crop field trials (MRID 45252211) on bell peppers conducted in CA (2 trials), FL (1 trial), IN (1 trial), NC (1 trial), and TX (1 trial) and on non-bell peppers conducted in CA (1 trial), NM (1 trial), and TX (1 trial). The combined residues of diflubenzuron and its metabolites CPU and PCA were <0.065-<0.281 ppm in/on bell peppers and <0.229-<0.997 ppm in/on non-bell peppers harvested 7 days following the last of five foliar applications of the 25% WP formulation at 0.125 lb ai/A/application for a total seasonal application rate of ~0.625 lb ai/A (1x the maximum proposed seasonal rate for peppers).

Under the current petition, a tolerance of 1.0 ppm has been proposed for the combined residues of diflubenzuron and metabolites convertible to PCA, expressed as diflubenzuron, in/on peppers. The HED MARC has concluded (DP Barcode D272976, 5/31/01, G. Kramer) that the residues of concern in plants are diflubenzuron and its metabolites PCA and CPU. Based on the submitted data, the proposed tolerance of 1.0 ppm for peppers is appropriate; however, the tolerance should be expressed in terms of "the combined residues of diflubenzuron [N-[[[4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide] and its metabolites 4-chloroaniline and 4-chlorophenylurea." A revised Section F should be submitted reflecting the change in tolerance expression and changing the commodity definition to "pepper."

No residue decline data were submitted. HED generally requires residue decline data when a pesticide is applied when the edible portion of the crop has formed and/or it is clear that quantifiable residues may occur on food or feed commodities at the earliest harvest time. However, decline data were submitted with the stone fruit residue trials (45252206.der.wpd). These data do demonstrate that residues generally declined from the 14-day PHI to the 28-day PHI. HED is willing to translate these data to peppers and concludes that additional residue decline data on peppers will not be required.

The crop field trials for peppers are classified acceptable and satisfy the guideline requirement for crop field trials (Residue Chemistry Guidelines OPPTS 860.1500).

Stone Fruits (except cherries)

Uniroyal has submitted the results from supervised crop field trial studies (MRIDs 45252206-45252208) in peaches conducted in 1997 and 1998 in CA (3 trials), GA (1 trial), MI (1 trial), NC (1 trial), OK (1 trial), PA (1 trial), and SC (1 trial), and in plums conducted in 1998 in CA (3 trials), MI (1 trial), and OR (1 trial). The combined residues of diflubenzuron, and its metabolites CPU and PCA in/on peaches and plums collected 78-196 days following the last of two foliar applications made at

dormancy and at petal fall of the 25% WP, 80% WDG, and/or 2 lb/gal FLC formulations in side-by-side trials for a total seasonal application rate of ~0.75 lb ai/A (1.5x the maximum proposed seasonal rate for stone fruits), were less than the combined method LOQs (<0.065 ppm in/on peaches and <0.060 ppm in/on plums).

Under the current petition, tolerances have been proposed for the combined residues of diflubenzuron and metabolites convertible to PCA, expressed as diflubenzuron, in/on "stonefruit (except cherries)" at 0.05 ppm. The HED MARC has concluded (DP Barcode D272976, 5/31/01, G. Kramer) that the residues of concern in plants are diflubenzuron and its metabolites PCA and CPU. Based on the submitted data for peaches and plums, the proposed tolerance of 0.05 ppm for stone fruits (excluding cherries) is inappropriate. The tolerance should be established at 0.07 ppm, reflecting the highest level of the combined method LOQs for diflubenzuron, CPU, and PCA, and should be expressed in terms of "the combined residues of diflubenzuron [N-[[4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide] and its metabolites 4-chloroaniline and 4-chlorophenylurea." A revised Section F should be submitted reflecting the change in tolerance expression and changing the commodity definition to "fruit, stone, group, except cherries."

With respect to the side-by-side trials conducted in peaches and plums, because residues were below the method LOQs in all samples from the side-by-side trials, no differences were observed in residue levels following treatment with the 25% WP, the 80% WDG, or the 2 lb/gal FLC formulation.

The crop field trials for peaches and plums are classified as acceptable and satisfy the guideline requirement for crop field trials (Residue Chemistry Guidelines OPPTS 860.1500).

Tree Nuts

Uniroyal Chemical Company has submitted the results from supervised crop field trials studies (MRIDs 45252209 and 45252210) in almonds conducted in CA (5 trials) and pecans conducted in GA (2 trials), LA (1), NM (1), and OK (1). Samples of almond and pecan nutmeats and hulls were collected 27-28 days following the last of four foliar applications of diflubenzuron at 0.5 lb ai/A/application (applications 1 and 4) and 0.25 lb ai/A/application (applications 2 and 3) for a total seasonal application rate of ~1.5 lb ai/A (1.5x the maximum proposed seasonal rate for tree nuts). For the almond field trials, side-by-side trials were conducted at one field site using the 25% WP formulation, the 2 lb/gal FLC formulation, and the 80% WDG formulation; the 25% WP formulation alone was used at the remaining field sites. For the pecan field trials, side-by-side trials using all three formulations were conducted at one GA site

and the LA and OK sites, and the 2 lb/gal FlC formulation alone was used at the remaining GA site and the NM site. Combined residues of diflubenazuron, and its metabolites CPU and PCA were less than the combined method LOQs (<0.060 ppm) in/on almond and pecan nutmeats and <0.987-<5.547 in/on almond hulls.

Under the current petition, tolerances have been proposed for the combined residues of diflubenazuron and metabolites convertible to PCA, expressed as diflubenazuron, in/on "tree nuts and pistachios" at 0.05 ppm and in/on almond hulls at 5.0 ppm. The HED MARC has concluded (DP Barcode D272976, 5/31/01, G. Kramer) that the residues of concern in plants are diflubenazuron and its metabolites PCA and CPU. Based on the submitted data for almond and pecan nutmeats, the proposed tolerance of 0.05 ppm for tree nuts and pistachios is not appropriate. The tolerance should be established at 0.06 ppm, the level of the combined method LOQs for diflubenazuron, CPU, and PCA, and should be expressed in terms of "the combined residues of diflubenazuron [N-[[4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide] and its metabolites 4-chloroaniline and 4-chlorophenylurea." HED has concluded that pistachios are to be included as a member of the tree nuts crop group and that field residue data for almonds will be translatable to pistachios. Pending issuance of the Federal Register Notice revising the Crop Group Regulation, tolerances for pistachios are to be listed separately from the crop group but the tolerance is to be established at the same level as the crop group (Memorandum dated 9/20/01, B. Schneider). A revised Section F should be submitted reflecting the change in tolerance expression and proposing separate tolerances for "nut, tree, group" and "pistachio" at 0.06 ppm each.

The trials were conducted at 1.5x the maximum proposed application rate. However, the final application of the test substance (typically the application that determines the residues in the crop at harvest) was made at the maximum per application rate. Because the per application rate was 1x, the crop field trials for tree nuts are classified as acceptable. The data satisfy the guideline requirement for crop field trials (Residue Chemistry Guidelines OPPTS 860.1500) for tree nuts. Based on the results of these trials, the petitioner should propose a tolerance of 6.0 ppm for the combined residues of diflubenazuron, CPU, and PCA in/on "almond, hulls." Concomitant with the establishment of the tree nut group tolerance, the established tolerance for walnuts of 0.1 ppm should be revoked. Data submitted in support of an SLN use of diflubenazuron in CA (CB No. 3059, F. Boyd, 3/11/88), indicated that residues of diflubenazuron were less than the method LOQ (<0.05 ppm) in/on walnuts harvested 28 days after the last of three applications of a 25% WP formulation at 0.5 lb ai/A/application for a total seasonal rate of 1.5 lb ai/A (1x the maximum seasonal rate for walnuts under SLN CA940004; 1.5x the maximum proposed seasonal rate for tree

nuts). Based on these data, the proposed tolerance for the tree nut group will be adequate to cover residues of diflubenzuron in/on walnuts.

With respect to the side-by-side trials conducted in almonds and pecans, no significant differences were observed in residue levels in almond or pistachio hulls (discussed here for informational purposes only) following treatment with the 25% WP, the 80% WDG, or the 2 lb/gal FlC formulation in the side-by-side trials. Residues were <2.883 and <3.651 ppm, <3.409 and <5.547 ppm, and <2.921 and <3.140 ppm, respectively, in/on almond hulls following treatment with the 25% WP, the 80% WDG, and the 2 lb/gal FlC formulations. Residues were <0.080-0.771 ppm (n=6), <0.065-<0.381 ppm (n = 6), and <0.113-<1.392 ppm (n = 10), respectively, in/on pecan hulls following treatment with the 25% WP, the 80% WDG, and the 2 lb/gal FlC formulations.

OPPTS GLN 860.1520: Processed Food/Feed

In support of the proposed foliar use of diflubenzuron on stone fruit, Uniroyal has submitted a plum (prune) processing study (MRID 45252208); refer to D277691, DER 860.1520 for review of these data. Detectable residues of diflubenzuron were observed at 0.136-0.187 ppm in/on plums collected 147 days following two foliar applications of the 25% WP formulation made at dormancy (2.0 lb ai/A) and at petal fall (1.0 lb ai/A) for a total application rate of 3.0 lb ai/A (6x the maximum proposed seasonal rate for stone fruits); residues of CPU and PCA were below the LOQ (<0.005 ppm). The plums were processed into prunes according to simulated commercial procedures. Analysis indicated that residues of diflubenzuron reduced (0.8x) in prunes; therefore, a tolerance for residues of diflubenzuron in prunes is not required.

This processed food/feed study is classified acceptable and satisfies the guideline requirement for a processing study (Residue Chemistry Guidelines OPPTS 860.1520).

OPPTS GLN 860.1480: Meat/Milk/Poultry/Eggs

Although almond hulls are considered a feed commodity, no impact is expected on the dietary burden resulting from the proposed use on almonds because the contribution of almond hulls to the livestock diet is minor compared to the existing exposure from registered uses on grasses, soybeans, and cotton. HED concludes that the current tolerances on meat, milk, poultry, and eggs are adequate to cover the additional residues resulting from the proposed uses on almonds. Tolerances of 0.05 ppm have been

established for residues of diflubenzuron per se in eggs, milk, livestock fat, meat, and meat by-products.

Under Section G of the subject petition, Uniroyal has proposed to increase the established tolerance for meat byproducts from 0.05 to 0.15 ppm in connection with the increase in the tolerance for rangeland grass from 3.0 ppm to 6.0 ppm (65 FR 47882, Aug. 4, 2000). HED previously determined that diflubenzuron residues (parent only) in ruminant liver would be <0.05 ppm, PCA would be <0.002 ppm and CPU would be <0.06 ppm (PP#5E4499, Memo Jerry Stokes, 2/28/96). Thus, the proposed tolerance of 0.15 ppm is appropriate for the combined residues of diflubenzuron and its metabolites CPU and PCA. The tolerance should be expressed in terms of "the combined residues of diflubenzuron [N-[[[4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide] and its metabolites 4-chloroaniline and 4-chlorophenylurea." A revised Section F should be submitted reflecting the change in tolerance expression and changing the commodity definition to "Cattle, Meat Byproducts; Goat, Meat Byproducts; Hog, Meat Byproducts; Horse, Meat Byproducts and Sheep, Meat Byproducts."

OPPTS GLN 860.1850: Confined/Field Accumulation in Rotational Crops

The Residue Chemistry Chapter of the Diflubenzuron RED dated 3/16/95 concluded that the nature of the residue in rotational crops is adequately understood for purposes of reregistration. The available study, though inadequate, indicated that residues of diflubenzuron and CPU might exceed 0.01 ppm in rotational crops planted up to 4 months and in cereal grains planted up to 12 months after a 1x application of diflubenzuron to the primary crop.

Data from two limited rotational field trials were submitted in conjunction with a rice petition (PP#8F4925; DP Barcodes D253043, D253041, D244487, D251221, and D251609, 2/17/99, G. Kramer). Cotton was selected as the primary crop in both studies because it had the highest labeled use rate (0.375 lb ai/A/season) of any rotatable crop. In the studies, lettuce, turnips, and wheat were planted as representative rotational crops at plantback intervals of 30, 45, 60, 90, 120, 180, and 365 days following the final application of diflubenzuron. Although residues of diflubenzuron or CPU were found above the LOQ (0.01 ppm) in a number of samples of lettuce, turnip roots and tops, and wheat grain and straw, the residue levels in these samples were generally low (≤ 0.06 ppm), and the associated control samples usually bore apparent residues at similar levels. Given the low number of samples bearing residues of diflubenzuron or CPU and the low levels (0.01-0.06 ppm) of these residues, HED concluded that quantifiable residues of diflubenzuron, CPU, and PCA were unlikely to occur in rotated

crops planted at least 30 days following the final application of diflubenzuron to the primary crop, and that the data indicated that tolerances for diflubenzuron residues in rotational crops would not be required provided the Dimilin labels specified a restriction for the planting of rotation crops of at least 30 days.

Peppers are the only rotatable crop for which foliar use of diflubenzuron is being proposed under the current petition. The maximum proposed seasonal rate for peppers of 0.625 lb ai/A is 1.7x the seasonal application rate of 0.375 lb ai/A that was used in the limited rotational field trials. If the petitioner wishes to maintain a 30-day plantback interval for peppers on diflubenzuron labels, then new limited field trials should be conducted reflecting application of diflubenzuron at 0.625 lb ai/A; otherwise, a 12-month plantback interval should be established.

Other Considerations:

Codex and Mexican maximum residue limits (MRLs) are established for residues of diflubenzuron per se in/on plums (including prunes) at 1 ppm. Mexican MRLs are established for residues of diflubenzuron per se. Use of diflubenzuron in Canada is limited to mosquito control; therefore, no Canadian MRLs have been established. Based on the current tolerance expression the Codex and U.S. tolerance definitions are not compatible.

AGENCY MEMORANDA CITED

DP Barcode: D209032

Subject: Diflubenzuron. Chemistry Chapter of the Reregistration Eligibility Document. Reregistration Case No. 0144. Chemical No. 108201.

From: S. Knizner

To: S. Jennings and K. Whitby/L. Kutney

Date: 3/16/95

MRIDs: None

DP Barcode: D216357

Subject: PP#5E4499. Diflubenzuron. Geographical Expansion For Use Of Dimilin 25W and Dimilin 2F Formulations in/on Rangeland Grass. Grasshopper Control.

From: J. Stokes

To: H. Jamerson

Date: 2/27/96

MRIDs: 43657901 and 43657902

DP Barcode: D240107

Subject: PP#8F4925. Diflubenzuron (Dimilin® 2L, EPA Reg. #400-461) on Rice. Evaluation of Residue Data and Analytical Methods.
From: G. Kramer
To: T. Levine
Date: 6/23/98
MRIDs: 44486401, and 44399301-44399306

DP Barcode: D251484

Subject: PP#8F4925. Diflubenzuron (Dimilin® 2L, EPA Reg #400-461) on Rice. Request for Petition Method Validation (PMV).
From: J. Rowell
To: D. Marlow
Date: 12/15/98
MRIDs: 44399303, 44399306, 44695001, and 44695002

DP Barcode: D253043, D253041, D244487, D251221, and D251609

Subject: PP#8F4925. Diflubenzuron (Dimilin® 2L, EPA Reg #400-461) on Rice. Amendments of 8/19/98, 11/20/98, 12/3/98, 1/21/99, 1/27/99 & 2/3/99. Analytical Method for Metabolites, Revised Label, Additional Residue, Storage Stability, and Rotational Crop Data.
From: G. Kramer
To: M. Johnson/A. Sibold
Date: 2/17/99
MRIDs: 44577601, 44689701, 44689702, 44699201, 44692701, 44692703, 44695001, 44695002, and 44707401

DP Barcode: D272978

Subject: PP#6E06167. Diflubenzuron (Dimilin® 2L, EPA Reg #400-461) in/on Pears. Evaluation of Residue Data and Analytical Methods.
From: G. Kramer
To: S. Brothers/R. Forrest
Date: 4/3/01
MRIDs: 45119601 and 45119602

DP Barcode: D272976

Subject: Health Effects Division (HED Metabolism Assessment Review Committee (MARC) Meetings of 2/20/01 & 5/8/01. Diflubenzuron. Residues of Concern for Cancer Risk Assessment.
From: G. Kramer/G. Reddy
To: Y. Donovan
Date: 5/31/01
MRIDs: None

DP Barcode: None

Subject: Reviewer's Guide and Summary of HED ChemSAC Approvals
for Amending Commodity Definitions [40 CFR §179.1(h)]
and Crop Group/Subgroups [40 CFR §180.41].

From: B. Schneider

To: H. Jamerson

Date: 9/20/01

MRIDs: None

INTERNATIONAL RESIDUE LIMIT STATUS			
Chemical Name: N- [[[4-chlorophenyl] amino]carbonyl]-2,6- difluorobenzamide	Common Name: Diflubenzuron	X Proposed tolerance X Reevaluated tolerance <input type="checkbox"/> Other	Date: 11/01
Codex Status (Maximum Residue Limits)		U. S. Tolerances	
<input type="checkbox"/> No Codex proposal step 6 or above <input type="checkbox"/> No Codex proposal step 6 or above for the crops requested		Petition Number: PP#1F06235 DP Barcode: D277691 Other Identifier:	
Residue definition (step 8/CXL): diflubenzuron		Reviewer/Branch: G. Kramer/RAB1 Residue definition: Combined residues of diflubenzuron and its metabolites convertible to PCA, expressed as diflubenzuron	
Crop (s)	MRL (mg/kg)	Crop(s)	Tolerance (ppm)
		Almond hulls	5.0
		Peppers	1.0
Plums (including prunes)	1	Stonefruit (except cherries)	0.05
		Tree nuts and pistachios	0.05
Edible offal (mammalian)	0.05 (*)	Meat by-products (proposed increase)	0.15
Limits for Canada		Limits for Mexico	
X No Limits <input type="checkbox"/> No Limits for the crops requested		<input type="checkbox"/> No Limits X No Limits for the crops requested	
Residue definition: N/A. Non-crop use only (mosquito control).		Residue definition: Diflubenzuron	
Crop(s)	MRL (mg/kg)	Crop(s)	MRL (mg/kg)
Notes/Special Instructions: S. Funk, 12/03/01.			

Rev. 1998

DIFLUBENZURON
PC Code 108201; Case 293515
(DP Barcode D277691)

Storage Stability Data, Peppers;
OPPTS 860.1380

January 30, 2002

Contract No. 68-W-99-053

Submitted to:
U.S. Environmental Protection Agency
Arlington, VA

Submitted by:
Dynamac Corporation
20440 Century Boulevard, Suite 100
Germantown, MD 20874

Chemical Name Diflubenzuron
PC Code: 108201
EPA Barcode: D277691

Storage Stability Data
GL: OPPTS 860.1380
PP#1F06235

MRID: 45252211
Case No.: 293515
Submission: S602900

EPA Reviewer: George F. Kramer, Ph.D., Date: 27-FEB-2002

STUDY TYPE: Storage Stability Data; OPPTS 860.1380

TEST MATERIAL: Diflubenzuron (N-[[[(4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide); CPU (4-chlorophenylurea); and PCA (p-chloroaniline)

SYNONYMS: Diflubenzuron Trade names: Dimilin, Vigilante, Micromite, Adept

CITATION: 45252211 Gaydosh, K.A.; Puhl, J.F. (2001) Dimilin® 25W on Bell and Non-Bell Peppers: Magnitude of the Residue Study. Study No.: RP-97016. Unpublished study submitted by Uniroyal Chemical Company, Inc. 1115 p.

SPONSOR: Uniroyal Chemical Company, Inc.

EXECUTIVE SUMMARY:

In the freezer storage stability study (MRID 45252211) that was conducted concurrently with the diflubenzuron pepper field trials (PP#1F06235), samples of homogenized bell peppers were spiked separately with diflubenzuron, CPU, and PCA at levels of 0.5, 0.1 and 0.1 ppm, respectively, and were stored frozen for 12 months. The storage stability data indicate that residues of diflubenzuron *per se* were relatively stable in bell peppers stored frozen for up to 12 months. Residues of CPU declined ~20% following 3 months of frozen storage but did not decline further through the study. Residues of PCA in fortified bell pepper samples declined ~30% following 1 month of frozen storage, and continued to decline through the study; following 12 months of frozen storage residues had declined ~70%.

Storage stability samples were analyzed for residues of diflubenzuron, CPU, and PCA using GC/ECD methods for diflubenzuron and CPU, and a GC/MS method for PCA. Based on the available method validation and concurrent recovery data, the methods are adequate for data collection in bell peppers.

Raw agricultural commodity (RAC) samples from the pepper field trial studies (45252211.der.wpd) were stored frozen for up to 357 days (~12 months) prior to analysis for residues of diflubenzuron, CPU, and PCA. The submitted freezer storage stability study is sufficient to support the storage intervals and conditions of samples from the pepper field trial studies.

This freezer storage stability study is classified acceptable and satisfies the guideline requirement for a freezer storage stability study (Residue Chemistry Guidelines OPPTS 860.1380).

COMPLIANCE: Signed and dated GLP, Quality Assurance and Data Confidentiality statements were provided. GLP deviations were reported concerning inspection and equipment SOPs, QA auditors, and signature dates.

Chemical Name Diflubenzuron
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EPA Barcode: D277691

Storage Stability Data
GL: OPPTS 860.1380
PP#1F06235

MRID: 45252211
Case No.: 293515
Submission: S602900

I. MATERIALS AND METHODS

MATERIALS:

1. Test Compounds:

Chemical name

Common name: Diflubenzuron

IUPAC: 1-(4-Chlorophenyl)-3-(2,6-difluorobenzoyl)urea

CAS name: Benzamide, -[[[(4-chlorophenyl)amino]carbonyl]-2,6-difluoro-

Developmental (Company) name: Not available

Purity: 99.9%

Spiking level(s): 0.5 ppm

Chemical name

Common name: CPU

IUPAC: 4-Chlorophenyl urea

CAS name: Not available

Developmental (Company) name: Not available

Purity: 99.7%

Spiking level(s): 0.1 ppm

Chemical name

Common name: PCA

IUPAC: p-Chloroaniline or 4-chloroaniline

CAS name: Benzenamine, 4-chloro

Developmental (Company) name: Not available

Purity: 100%

Spiking level(s): 0.1 ppm

2. Test Commodity:

Identification of RAC

Crop: Pepper

Type: Bell

Variety: Jupiter

Botanical name: Not available

Crop part(s) or processed commodity: Whole fruit

Developmental stage (s)/general condition: Mature

Treatment/preparation of RAC or processed commodity sample(s): Ground/
homogenized with dry ice in a Hobart cutter-mixer.

Sample form (i.e. extract/macerate/etc.): Homogenate

3. Methods:

Experimental design (no. of test commodities, test substances, etc.):

Test procedures

Spiking procedure

Spiked: Untreated samples from a CA field trial were separately spiked with diflubenzuron, CPU, and PCA at 0.5, 0.1, and 0.1 ppm, respectively. Fresh fortification samples were separately spiked with diflubenzuron, CPU, and PCA at 0.20 ppm (0.4 ppm for diflubenzuron

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0-day) on the day of analysis. Stock solutions for fortification were prepared in hexane:acetone (9:1, v:v) for diflubenzuron; in acetonitrile for CPU; and in hexane for PCA based on the fortification procedures of the methods.

Storage conditions

Temperature: Frozen (<-10 C)
Humidity: Not reported
Lighting: Not reported
Container type(s)/size: Not reported
Duration: 12 months

Sampling (sampling procedure at zero time and at regular intervals

thereafter): Samples were analyzed for all three analytes at storage intervals of 0, ~1, ~3, ~6, and ~12 months. Individual samples were prepared for each sampling interval at initiation of the study.

Dates of sample preparation: Diflubenzuron: 4/15/98 (0-day), 4/9/98 (1-, 3-, 6-, and 12-month samples); CPU: 4/10/98; PCA: 4/8/98.

Methods of residue analysis:

Analytical method reference no.: Analyzed for residues of diflubenzuron, CPU and PCA using three separate GC methods.

Deviations from analytical procedure used for residue analysis of field trial samples or processed commodities: None

Analytical method:

Diflubenzuron - GC/ECD

Samples were homogenized and extracted with dichloromethane and vacuum filtered. The filtrate was evaporated to dryness at ~35 C, and residues were redissolved in dichloromethane. Petroleum ether was added, and the solution was applied to a Florisil column for cleanup. Residues were eluted from the Florisil column with 20% acetone in petroleum ether, evaporated to dryness, and redissolved in 85% phosphoric acid. The acidic solution was heated at slow reflux for 30 minutes, cooled, and the hydrolysate was extracted with hexane. The aqueous phase was diluted with 50% NaOH in an ice bath to pH ≥ 12. The resulting alkaline solution was extracted with hexane (3x). Hexane extracts were combined, and the volume was adjusted to 200 mL with additional hexane. Heptafluorobutyric anhydride (HFBA) was added to an aliquot of the hexane extract. After 10 minutes, water was added, and the organic phase collected for analysis. Using this method, residues of diflubenzuron are converted to p-chloroaniline (PCA), which is then derivatized with HFBA. The HFBA-derivatized PCA was quantitated by GC analysis using electron capture detection (ECD); external calibration curves of diflubenzuron standards (HFBA-derivatized PCA) and peak area comparisons were utilized for quantitation. Residues were calculated as diflubenzuron using a molecular weight conversion factor. The reported method limit of quantitation (LOQ) was 0.05 ppm for diflubenzuron in peppers.

CPU - GC/ECD

Samples were homogenized and extracted with ethyl acetate, then vacuum filtered. The filtrate was evaporated to dryness at ~35 C, and residues were redissolved in acetone. Petroleum ether was added, and the solution was applied

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to a deactivated silica gel column for cleanup. Residues were eluted from the silica column with ethanol:petroleum ether (30:70, v:v), evaporated to dryness, redissolved in hexane, evaporated to dryness again, and redissolved in acetonitrile (ACN). HFBA was added to a small aliquot of the ACN-suspended residues. After 10 minutes, water, saturated sodium carbonate, and hexane were added, and the organic phase was collected for analysis. Using this method, residues of CPU are derivatized with HFBA. The HFBA-derivatized CPU was quantitated by GC analysis using ECD detection; external calibration curves of HFBA-derivatized CPU standards and peak area comparisons were utilized for quantitation. The reported method LOQ was 0.01 ppm for CPU in peppers.

PCA - GC/MS

Samples were homogenized, then mixed with solutions of ^{12}C -PCA (fortified samples only) and ^{13}C -PCA (internal standard). After 5 minutes 0.1 N HCl was added, and the mixture was shaken at $\sim 60^\circ\text{C}$ in a water bath for 30 minutes. The cooled mixture was centrifuged, and the resulting supernatant was filtered. The pellet was further extracted with 0.1 N HCl (2x), then shaken for 20 minutes, centrifuged, and filtered. The filtrates were combined, diluted with aqueous 50% NaOH to $\text{pH} > 12$, then combined with solid NaCl. The solution was partitioned with hexane (3x) and centrifuged. The hexane phases were combined and partitioned with 0.1 N HCl (2x). Aqueous 50% NaOH was added to the combined acid phases until a $\text{pH} \geq 12$ was achieved, and the extract was partitioned with hexane containing sodium sulfate (3x). The combined hexane phases were applied to a GRM Florisil column for further cleanup. Residues were eluted from the Florisil column with 20% acetone in hexane, and HFBA was added to the eluate. After 10 minutes, water and saturated sodium carbonate were added, and the organic phase was collected for analysis. Using this method, residues of PCA are derivatized with HFBA. The HFBA-derivatized PCA was quantitated by GC/MS analysis with selective ion monitoring (SIM) of ions 323, 329, 126, and 132. Identification of PCA was by comparison of its retention time with that of the internal standard (^{13}C -PCA), and quantification was by integration of the peak area for ^{12}C -PCA relative to ^{13}C -PCA. In addition, comparison of the peak area of ^{12}C -PCA with the external standard linearity curve was used for quantitation (confirmation technique). Area ratio linearity curves were used to determine that the response was linear over the range of detection. The reported method LOQ was 0.005 ppm for PCA in peppers.

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II. RESULTS

TABLE 1. Stability of Diflubenzuron and its Metabolites CPU and PCA Residues in Peppers Stored Frozen.

Commodity	Analyte	Spiked Residue Level ¹ (ppm)	Storage Period (days) ²	Fresh Spike Recovery ³	Apparent Recovery in Stored Sample	Corrected Recovery in Stored Sample ⁴
Pepper, bell	Diflubenzuron	0.5	6	70, 73 (72)	--	--
			36	117, 137 (127)	131, 138	103, 109
			95	77, 77 (77)	63, 72, 74	82, 94, 96
			180	78, 80 (79)	76, 81, 81	96, 103, 103
			369	81, 87 (84)	74, 79, 84	88, 94, 100
Pepper, bell	CPU	0.100	3	89.1, 93.5 (91)	--	--
			34	71	63, 65	89, 92
			90	103, 109 (106)	69, 78, 84	65, 74, 79
			187	82, 91 (87)	64, 66, 66	74, 76
			369	69, 83 (76)	54, 55, 57	71, 72, 75
Pepper, bell	PCA	0.100	1	73, 96 (85)	--	--
			37	92, 97 (95)	53, 57, 59	56, 60, 62
			93	101, 101 (101)	46, 46, 52	46, 46, 51
			188	75, 76 (76)	31, 31, 32	41, 41, 42
			370	87, 87 (87)	18, 19, 20	21, 22, 23

¹ Fresh fortification samples were spiked at 0.2 ppm for all intervals except that the 0-day sample for diflubenzuron was spiked at 0.4 ppm.

² Storage period is days from fortification to analysis; all samples were analyzed within 0-7 days of extraction.

³ Average recoveries are reported in parentheses.

⁴ Corrected recoveries of stored samples were calculated by the study reviewer using the average fresh fortification recovery.

Comments:

Corrected recoveries of diflubenzuron in fortified bell pepper samples were 88-100% following frozen storage for ~12 months. These recoveries were comparable to the average fresh fortification recoveries of 85% at the 12-month interval and the 0-day fresh fortification recovery of 72%. These data indicate that residues of diflubenzuron are relatively stable in bell peppers stored frozen for up to 12 months.

Corrected recoveries of CPU in fortified bell pepper samples were 65-79% following 3 months of frozen storage, but did not decline further; following 12 months of frozen storage recoveries were 71-75%. The petitioner noted that stored sample recoveries for CPU were consistently lower than the fresh fortification recoveries, and that the overall variability associated with the CPU analytical method may have been a contributing factor to the apparent decline. These data indicate that residues of CPU are

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relatively stable in bell peppers stored frozen for up to 12 months after an initial decline of ~20% following 3 months of frozen storage.

Corrected recoveries of PCA in fortified bell pepper samples decreased ~30% following 1 month of frozen storage, and continued to decline, with corrected recoveries of 46-51% in samples stored for ~3 months, 41-42% in samples stored for ~6 months, and 21-23% in samples stored for ~12 months. These data indicate that residues of PCA decline in bell peppers by ~30% following 1 month of frozen storage and ~70% following 12 months frozen storage.

RAC samples from the pepper field trial studies (45252211.der.wpd) were stored frozen for up to 357 days (~12 months) prior to analysis for residues of diflubenzuron, CPU, and PCA. The submitted freezer storage stability study is sufficient to support the storage intervals and conditions of samples from the pepper field trial studies.

III. FINAL SUMMARY

In the freezer storage stability study (MRID 45252211) that was conducted concurrently with the diflubenzuron pepper field trials (PP#1F06235), samples of homogenized bell peppers were spiked separately with diflubenzuron, CPU, and PCA at levels of 0.5, 0.1 and 0.1 ppm, respectively, and were stored frozen for 12 months. The storage stability data indicate that residues of diflubenzuron *per se* were relatively stable in bell peppers stored frozen for up to 12 months. Residues of CPU declined ~20% following 3 months of frozen storage but did not decline further through the study. Residues of PCA in fortified bell pepper samples declined ~30% following 1 month of frozen storage, and continued to decline through the study; following 12 months of frozen storage, residues had declined ~70%.

Storage stability samples were analyzed for residues of diflubenzuron, CPU, and PCA using GC/ECD methods for diflubenzuron and CPU, and a GC/MS method for PCA. Based on the available method validation and concurrent recovery data, the methods are adequate for data collection in bell peppers.

RAC samples from the pepper field trial studies (45252211.der.wpd) were stored frozen for up to 357 days (~12 months) prior to analysis for residues of diflubenzuron, CPU, and PCA. The submitted freezer storage stability study is sufficient to support the storage intervals and conditions of samples from the pepper field trial studies.

This freezer storage stability study is classified acceptable and satisfies the guideline requirement for a freezer storage stability study (Residue Chemistry Guidelines OPPTS 860.1380).

IV. STUDY DEFICIENCIES

No deficiencies were identified.

DIFLUBENZURON
PC Code 108201
(DP Barcode D277691)

Crop Field Trials, Stone Fruits;
OPPTS 860.1500

January 30, 2002

Contract No. 68-W-99-053

Submitted to:
U.S. Environmental Protection Agency
Arlington, VA

Submitted by:
Dynamac Corporation
20440 Century Boulevard, Suite 100
Germantown, MD 20874

Chemical Name Diflubenzuron
PC Code: 108201
EPA Barcode: D277691

Crop Field Trials
GL: OPPTS 860.1500
PP#1F06235

MRID: 45252206-45252208
Case No.: 293515
Submission: S602900



EPA Reviewer: George F. Kramer, Ph.D., Date: 27-FEB-2002

STUDY TYPE: Crop Field Trials - Stone Fruits; OPPTS 860.1500

TEST MATERIAL: Diflubenzuron (N-[[[(4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide); CPU (4-chlorophenylurea); and PCA (parachloroaniline)

FORMULATION AND TYPE: Dimilin® 2 lb/gal flowable concentrate (FIC) formulation (EPA Reg. No. 400-461); Dimilin® 80% wettable granular (WG) formulation (EPA File Symbol No. 400-XXX); and Dimilin® 25% wettable powder (WP) formulation (EPA Reg. No. 400-465)

SYNONYMS: Diflubenzuron Trade names: Dimilin, Vigilante, Micromite, Adept

CITATION: 45252206 Gaydos, K.A. (1999) Dimilin® 25W in Peaches: Magnitude of the Residue. Study No.: RP-97008. Unpublished study submitted by Uniroyal Chemical Company, Inc. 517 p.

45252207 Gaydos, K.A. (2000) Dimilin® 25W, Dimilin® 80WG, and Dimilin® 2 L in Peaches: Magnitude of the Residue Study. Study No.: RP-98001. Unpublished study submitted by Uniroyal Chemical Company, Inc. 742 p.

45252208 Gaydos, K.A. (2000) Dimilin® 25W, Dimilin® 80WG, and Dimilin® 2 L in Plums and Prunes: Magnitude of the Residue Study. Study No.: RP-98002. Unpublished study submitted by Uniroyal Chemical Company, Inc. 370 p.

SPONSOR: Uniroyal Chemical Company, Inc.

EXECUTIVE SUMMARY:

In support of the proposed foliar use of diflubenzuron on stone fruits, Uniroyal has submitted the results from supervised crop field trial studies (MRIDs 45252206-45252208) in peaches conducted in 1997 and 1998 in CA (3 trials), GA (1 trial), MI (1 trial), NC (1 trial), OK (1 trial), PA (1 trial), and SC (1 trial), and in plums conducted in 1998 in CA (3 trials), MI (1 trial), and OR (1 trial). The combined residues of diflubenzuron, and its metabolites CPU and PCA in/on peaches and plums collected 78-196 days following the last of two foliar applications made at dormancy and petal fall of the 25% WP, 80% WDG, and/or 2 lb/gal FIC formulations in side-by-side trials for a total seasonal application rate of ~0.75 lb ai/A (1.5x the maximum proposed seasonal rate for stone fruits), were less than the combined method limits of quantitation (LOQ) (<0.065 ppm in/on peaches and <0.060 ppm in/on plums).

With respect to the side-by-side trials conducted with peaches and plums, because residues were below the method LOQs in all samples from the side-by-side trials, no differences were observed in residue levels following treatment with the 25% WP, the 80% WDG, or the 2 lb/gal FLC formulation.

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Based on the available method validation conducted prior to analysis of field samples and concurrent recovery data, the methods (GC/ECD for diflubenzuron, GC/ECD or HPLC/MS for CPU, and GC/MS for PCA) used to quantitate residues of diflubenzuron, CPU, and PCA are adequate for data collection in/on peaches and plums. For residues of diflubenzuron, *per se*, the validated method LOQs were 0.005 ppm for peaches from the 1997 trials and 0.05 ppm for peaches from the 1998 trials and plums. For residues of CPU, the validated method LOQs were 0.01 and 0.005 ppm for peaches from the 1998 trials and plums, respectively, analyzed by HPLC/MS, and 0.005 ppm for peaches from the 1997 trials analyzed by GC/ECD. For residues of PCA, the validated method LOQ was 0.005 ppm for PCA in/on peaches and plums. No interference was observed in representative chromatograms of control samples from the analysis of peaches and plums.

Because residues were below the LOQ in peaches and plums, the crop field trials for peaches and plums are classified as acceptable and satisfy the guideline requirement for crop field trials (Residue Chemistry Guidelines OPPTS 860.1500).

COMPLIANCE: Signed and dated GLP, Quality Assurance, and Data Confidentiality statements were provided. GLP deviations were reported concerning the test substance, weather, maintenance chemicals, and irrigation.

I. MATERIALS AND METHODS

Peach and plum samples were analyzed for residues of diflubenzuron, CPU, and PCA using a GC/ECD method for diflubenzuron, HPLC/MS and GC/ECD methods for CPU, and a GC/MS method with isotope dilution for PCA. Samples were analyzed by PTRL West (Richmond, CA). The GC/ECD method used for the quantitation of diflubenzuron is similar to PAM Vol II, Method I; the GC methods used for the quantitation of CPU and PCA are similar to those submitted previously for use on rice and subsequently submitted for petition method validation (PMV) as enforcement methods (PP#8F4925, D251484, 12/15/98, J. Rowell). Brief descriptions of the methods follow.

Diflubenzuron - GC/ECD

Samples of peaches and plums were analyzed for residues of diflubenzuron using a GC/ECD method entitled "Gas Chromatographic Determination of Diflubenzuron Residues in Apples Brussels Sprouts, and Artichokes." Samples were homogenized, then extracted with dichloromethane (2x) and vacuum filtered. The filtrates were combined, evaporated to dryness at ~35-45 C, and residues were redissolved in dichloromethane. Petroleum ether was added, and the solution was applied to a Florisil column for cleanup. Residues were eluted from the Florisil column with 20% acetone in petroleum ether, evaporated to dryness, and redissolved in 85% phosphoric acid. The acidic solution was heated at slow reflux for 30 minutes, cooled, and the hydrolysate was extracted with hexane. The aqueous phase was diluted with 50% NaOH in an ice bath to pH \geq 12. The resulting alkaline solution was extracted with hexane (3x). The hexane extracts were combined, and the volume was adjusted to 200 ml with additional hexane. Heptafluorobutyric anhydride (HFBA) was added to an aliquot of the hexane extract. After 10 minutes, water was added, and the organic phase was collected for analysis. Using this method, residues of diflubenzuron are converted to PCA and then derivatized with HFBA. The HFBA-derivatized PCA was quantitated by GC analysis using electron capture detection (ECD); external calibration curves of diflubenzuron standards (HFBA-derivatized PCA) and peak area comparisons were utilized for quantitation. Residues were calculated as diflubenzuron using a molecular weight conversion factor. The reported method LOQ was 0.005 for diflubenzuron in peaches (1997), and 0.05 ppm for diflubenzuron in peaches (1998) and plums.

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CPU - HPLC/MS

Samples of peaches from the 1998 trials and plums were analyzed for residues of CPU using an HPLC/MS method entitled "Dimilin 25W (Diflubenzuron): Non-food Aquatic Field Dissipation and Bioaccumulation in Aquatic Non-Target Organisms." Samples were homogenized and extracted with acetonitrile (ACN; 2x) and vacuum filtered or centrifuged. The filtrates/supernatants were combined, and the volume was adjusted with additional ACN. An aliquot was partitioned with hexane (2x), and the ACN phase was concentrated and partitioned twice again with hexane. The ACN phase was evaporated to dryness at ~40 C. Residues were redissolved in water and partitioned with ethyl acetate (2x). The ethyl acetate phases were combined, concentrated to dryness, and residues were redissolved in ACN and diluted with water to achieve a 1:4 ratio of ACN:water for cleanup through a C18 solid phase extraction (SPE) cartridge. Residues were eluted from the C18 SPE cartridge with ACN:water (1:1, v:v) and partitioned with hexane (2x). The ACN phase was evaporated to dryness, redissolved in diethyl ether:hexane (1:19, v:v), and applied to a silica SPE cartridge for further cleanup. Residues were eluted from the silica SPE cartridge with acetone:hexane (1:1, v:v) and evaporated to dryness. Residues were redissolved in ACN and diluted with water for HPLC analysis. CPU was quantitated by HPLC analysis using a Microsorb-C18 column, a step gradient mobile phase of ACN and water, and mass spectrometry (MS) detection; external calibration curves of CPU standards and peak area comparisons were utilized for quantitation. The reported method LOQ was 0.01 ppm for CPU in/on peaches and 0.005 ppm for CPU in plums.

CPU - GC/ECD

Samples of peaches from the 1997 trials were analyzed for residues of CPU using a GC/ECD method entitled "Gas Chromatographic Determination of Residues of Parachlorophenyl Urea (CPU) in Apples, Sugarbeets, Sugarbeet Leaves, Grass, Spinach, Onions, Wheat, Mushrooms, Protective Soil Layer, Compost, Cow Dung, and Calf Dung." Samples were homogenized and extracted with ethyl acetate (2x) and vacuum filtered. The filtrates were combined and extracted with water (2x). The ethyl acetate phase was evaporated to dryness at ~35 C, and residues were redissolved in acetone. Petroleum ether was added, and the solution was applied to a deactivated silica gel column for cleanup. Residues were eluted from the silica column with ethanol:petroleum ether (15:85 and 30:70, v:v), evaporated to dryness, redissolved in hexane, evaporated to dryness again, and redissolved in ACN. HFBA was added to a small aliquot of the ACN-suspended residues. After 10 minutes, water, saturated sodium carbonate, and hexane were added, and the organic phase was collected for analysis after ~30 minutes of shaking. Using this method, residues of CPU are derivatized with HFBA. The HFBA-derivatized CPU was quantitated by GC analysis using ECD detection; external calibration curves of HFBA-derivatized CPU standards and peak area comparisons were utilized for quantitation. The reported method LOQ was 0.005 ppm for CPU in peaches.

PCA - GC/MS

Samples of peaches and plums were analyzed for residues of PCA using a GC/MS method with isotope dilution entitled "Method Validation for 4-Chloroaniline (PCA) at Low Levels Using ^{13}C -PCA as Internal Standard in Rice and Rice Commodities." Samples were homogenized, then mixed with solutions of ^{12}C -PCA (fortified samples only) and ^{13}C -PCA (internal standard). After 5 minutes, 0.1 N HCl was added, and the mixture was shaken at ~60 C in a water bath for 30 minutes. The cooled mixture was centrifuged, and the resulting supernatant was filtered. The pellet was further extracted with 0.1 N HCl (2x), shaken for 20 minutes, centrifuged, and filtered. The filtrates were combined, diluted with aqueous 50% NaOH to pH >12, then combined with solid NaCl. The solution was partitioned with hexane (3x) and centrifuged. The hexane phases were combined and partitioned with 0.1 N HCl (2x). Aqueous 50%

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NaOH was added to the combined acid phases until a pH ≥ 12 was achieved, and the extract was partitioned with hexane containing sodium sulfate (3x). The combined hexane phases were applied to a GRM Florisil column for further cleanup. Residues were eluted from the Florisil column with 20% acetone in hexane, and HFBA was added to the eluate. After 10 minutes, water and saturated sodium carbonate were added, and the organic phase was collected for analysis. Using this method, residues of PCA are derivatized with HFBA. The HFBA-derivatized PCA was quantitated by GC/MS analysis with selective ion monitoring (SIM) of ions 323, 329, 126, and 132. Identification of PCA was by comparison of its retention time with the internal standard (^{13}C -PCA), and quantification was by integration of the peak area for ^{12}C -PCA relative to ^{13}C -PCA. In addition, comparison of the peak area of ^{12}C -PCA with the external standard linearity curve was used for quantitation (confirmation technique). Area ratio linearity curves were used to determine that the response was linear over the range of detection. The reported method LOQ was 0.005 ppm for PCA in peaches and plums.

Method validation was performed on peaches and plums at the laboratory prior to analysis of the field trial samples. Recoveries of diflubenzuron ranged 79-89% (mean = $84 \pm 3\%$) in/on six untreated plum samples, 85-102% (mean = $91 \pm 7\%$) in/on six untreated peach samples from the 1997 trials, and 65-101% (mean = $85 \pm 14\%$) in/on six untreated peach samples from the 1998 trials fortified at 0.005-1.0 ppm. Recoveries of CPU ranged 96-124% (mean = $108 \pm 11\%$) in/on six untreated plum samples and 94-107% (mean = $101 \pm 7\%$) in/on four untreated peach samples from the 1997 trials fortified at 0.005 and 0.01 ppm and analyzed by HPLC/MS (plums) or GC/ECD (peaches). Recoveries ranged 77-108% (mean = $98 \pm 13\%$) in/on five untreated peach samples from the 1998 trials fortified with CPU at 0.01 and 0.015 ppm and analyzed by HPLC/MS. High recoveries (136-142%) were obtained for peach samples fortified at 0.005 ppm and analyzed by HPLC/MS. Because these recoveries were not considered adequate for validation purposes, the validated LOQ was set at 0.01 ppm for residues of CPU in/on peaches from the 1998 trials. Recoveries of PCA ranged 77-104% (mean = $93 \pm 9\%$) in/on six untreated plum samples, 96-101% (mean = $100 \pm 2\%$) in/on four untreated peach samples from the 1997 trials, and 88-113% (mean = $101 \pm 10\%$) in/on six untreated peach samples from the 1998 trials fortified at 0.005 and 0.010 ppm. Concurrent method recovery data (presented below under 1.4.) were submitted. The validated method LOQs were 0.005 ppm for diflubenzuron in/on peaches from the 1997 trials, 0.05 ppm for diflubenzuron in/on peaches from the 1998 trials and plums; 0.01 and 0.005 ppm for CPU in/on peaches from the 1998 trials and plums, respectively; 0.005 ppm for CPU in/on peaches from the 1997 trials; and 0.005 ppm for PCA in/on peaches and plums.

Sample chromatograms of control and treated samples were provided; no interference was observed in the regions of diflubenzuron, CPU, or PCA in chromatograms for control samples of peaches and plums. The petitioner noted that in the GC/MS method validation for the 1997 peach study, a small interference was observed in control samples in the analysis of PCA residues which was most likely due to the presence of PCA in store-bought peaches. The calculated PCA residues in the control samples were subtracted from the residues in fortified samples (absolute recovery method).

1. Test Compound

Chemical name

IUPAC: 1-(4-Chlorophenyl)-3-(2,6-difluorobenzoyl)urea

CAS name: Benzamide, -[[(4-chlorophenyl)amino]carbonyl]-2,6-difluoro-

CAS #: 35367-38-5

Common name (ANSI, BSI or ISO): Diflubenzuron

Developmental (Company) name: Not available

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Chemical name

IUPAC: 4-Chlorophenyl urea
CAS name: Not available
CAS #: 140-38-5
Common name (ANSI, BSI or ISO): CPU
Developmental (Company) name: Not applicable (metabolite)

Chemical name

IUPAC: p-Chloroaniline or 4-chloroaniline
CAS name: Benzenamine, 4-chloro-
CAS #: 106-47-8
Common name (ANSI, BSI or ISO): PCA
Developmental (Company) name: Not applicable (metabolite)

2. Trial Numbers and Locations

Crop Stone Fruits	US Growing Regions						Total Trials
	1	2	5	6	10	12	
Submitted - Peaches	1	3	1	1	3	--	9
Requested - Peaches ¹	1	3	1	1	3	--	9
Submitted - Plums			1		3	1	5
Requested - Plums ¹	--	--	1	--	4	1	6

¹ OPPTS 860.1500, Table 5. Requested number of trials represents a 25% reduction in the number of trials for a representative commodity used to obtain a crop group tolerance.

Comments:

Geographic representation reflecting 1.5x the proposed use pattern is adequate for the stone fruit (except cherries) crop group. As required under OPPTS GLN 860.1500 (Tables 2 and 5) for the representative crops of the stone fruit crop group, excluding cherries, nine trials were conducted for peaches in Regions 1 (1 trial), 2 (3 trials), 5 (1 trial), 6 (1 trial), and 10 (3 trials). For plums, one trial each was conducted in Regions 5 and 12 as required by the guidelines; however, only three trials were conducted in Region 10 instead of four trials as required. HED concludes that, because all residues were below the method LOQ in both peach and plum samples, geographic representation is adequate for the purposes of this petition.

3. Proposed Label Use Pattern

80% WDG (Dimilin® 80WG; EPA File Symbol No. 400-XXX)
2 lb/gal FIC (Dimilin® 2L; EPA Reg. No. 400-461)

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Crop	Application					Comments/ Restrictions
	Method/ Timing	Maximum Single Application Rate	Maximum Number of Applications	Total Seasonal Rate	PHI (days)	
Stone Fruits (excluding cherries)	Foliar	0.25 lb ai/A	2	0.50 lb ai/A	Not specified	Applications after petal fall are prohibited. A minimum retreatment interval (RTI) of 21 days is specified. Applications are to be made in a minimum of 50 gal/A water for small trees (≤ 10 feet tall) or 100 gal/A for larger trees using ground equipment. Oil should be added to the finished spray when treating for peach twig borer.

The use pattern presented above is from specimen labels included in the administrative materials for PP#1F06235. The petitioner indicated that the 80% WDG formulation is identical to an 80% WDG formulation (Micromite® 80WG; EPA Reg. No. 400-487) that is currently registered for use on citrus in Florida only. HED notes that specimen labels included in MRIDs 45252206-45252208 for the 25% WP formulation (Dimilin® 25W; EPA Reg. No. 400-465) and the 80% WDG formulation did not include use directions for stone fruits.

The proposed use directions for the 80% WDG formulation (EPA File Symbol No. 400-XXX) and 2 lb/gal FIC formulation (EPA File Symbol No. 400-461) are adequate to allow HED an assessment of whether the submitted residue data reflect the maximum residues likely to occur in stone fruits (excluding cherries). Use directions were not provided for the 25% WP formulation.

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4. Analytical Method Validation (Concurrent)

Analyte (Method)	Spiking Level (mg/kg)	Recoveries obtained (%)	Range (%)	Mean recovery (SD)
Peaches (1997)				
Diflubenzuron (GC/ECD)	1.0	70, 71, 71, 74, 86, 90, 91, 92, 95, 95, 101, 101	70-101	87 (12)
CPU (GC/ECD)	0.05, 0.1	62, 73, 74, 87, 88, 94, 101, 101, 104, 108, 117	62-117	92 (17)
PCA (GC/MS)	0.005	91, 96, 97, 98, 99, 100, 100, 103, 103, 107	91-107	99 (4)
Peaches (1998)				
Diflubenzuron (GC/ECD)	0.05-0.10	63, 65, 65, 67, 79, 81, 85, 92, 92, 98	63-98	79 (15)
CPU (HPLC/MS)	0.01	77, 84, 92, 93, 100, 100, 104, 128	77-128	97 (15)
PCA (GC/MS)	0.005	61, 71, 72, 78, 81, 86, 87, 90, 91, 98	61-98	82 (11)
Plums				
Diflubenzuron (GC/ECD)	0.05, 0.10	70, 74, 78, 79, 83, 87, 87, 91	70-91	81 (7)
CPU (HPLC/MS)	0.005	67, 72, 85, 86, 86, 98, 107, 138	67-138	92 (22)
PCA (GC/MS)	0.005	90, 95, 96, 102, 103, 103, 106, 111,	90-111	101 (7)

Comments:

Based on the available method validation conducted prior to analysis of field samples and concurrent recovery data, the methods (GC/ECD for diflubenzuron, GC/ECD or HPLC/MS for CPU, and GC/MS for PCA) used to quantitate residues of diflubenzuron, CPU, and PCA are adequate for data collection in/on peaches and plums.

5. Storage Stability Conditions

Commodity	Storage Temperature (°C)	Duration (days)		
		DFB	CPU	PCA
Peaches (1997)	Frozen (temp. not specified)	68-293	76-402	279-351
Peaches (1998)	Frozen (temp. not specified)	35-204	323-407	34-285
Plums	<0 (laboratory)	127-200	266-326	231-298

Comments:

Peach and plum samples were frozen at the field site within 3.5 hours of harvest and were shipped frozen within 38 days of harvest to PTRL West (Richmond, CA) for residue analysis. Samples were stored frozen at the laboratory until sample preparation. Treated samples were analyzed within 18 days of extraction. Treated peach samples were stored for up to 293, 407, and 351 days (~10, 14, and 12

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months) prior to analysis for residues of diflubenzuron, CPU, and PCA, respectively. Treated plum samples were stored for up to 200, 326, and 298 days (~7, 11, and 10 months) prior to analysis for residues of diflubenzuron, CPU, and PCA, respectively.

Previously submitted storage stability data have demonstrated residues of diflubenzuron to be stable in various RACs for up to 12 months storage (Diflubenzuron Reregistration Eligibility Decision Document (RED), 3/16/95). PCA and CPU have been demonstrated to be unstable, degrading significantly after 1 and 3 months, respectively, in various RACs. Subsequent to the Diflubenzuron RED, storage stability data were submitted in conjunction with petitions for pears (PP#6E6167; D272978, 4/3/01, G. Kramer) and rice (PP#8F4925; DP Barcodes D253043, D253041, D244487, D251221, and D251609, 2/17/99, G. Kramer). These data indicate that residues of diflubenzuron *per se* were stable in/on pears for up to 2.5 months and in/on rice commodities (rice grain, straw, hulls, and bran) for up to 12 months; residues of CPU were relatively stable in/on rice commodities for up to 12 months, but decreased following 3 months storage in/on pears; and residues of PCA decreased significantly following 1 month storage in/on pears and rice commodities.

In addition, a storage stability study was conducted concurrently with pepper field trial studies submitted with the subject petition (PP#1F06235; 45252211.de2.wpd). The storage stability data indicate that residues of diflubenzuron *per se* and CPU are relatively stable in bell peppers stored frozen for up to 12 months. However, although CPU recoveries were within the acceptable range, some level of decline of CPU residues was observed (~20%) following 3 months of frozen storage. PCA recoveries in fortified bell pepper samples decreased significantly (~30%) following 1 month of frozen storage and decreased ~70% following 12 months of frozen storage.

The available storage stability data support the storage intervals and conditions for residues of diflubenzuron in/on peach and plum samples from the field trials. Although the available storage stability data indicate that residues in field samples stored for >1 month for PCA and >3 months for CPU, should be corrected for apparent decline during storage, correction for loss on storage would not significantly affect the results of the peach and plum field trial studies because residues of both metabolites were below the LOQs (<0.005-<0.01 ppm), which were significantly lower than the LOQ for diflubenzuron (0.05 ppm).

6. Application and RAC Information

Peaches

Whole peaches from 1997 field trials conducted in CA (2 trials) and NC (1) and from 1998 field trials conducted in CA (1), MI (1), GA (1), PA (1), OK (1), and SC (1) were collected at maturity following two applications of the 25% WP, 80% WDG, and/or 2 lb/gal FLC formulation made to dormant trees at ~0.50 lb ai/A and at petal fall at 0.25 lb ai/A, for a total seasonal application rate of 0.75 lb ai/A (1.5x the maximum proposed seasonal rate); RTIs were 19-40 days. For the 1997 trials, the applications were made in 82-100 gal/A (Sultana, CA and Knightdale, NC) or ~50 gal/A (Ripon, CA) with dormant oil added at 2-8 gal/A; for the 1998 trials, the first application was made in ~100 gal/A water with dormant oil added at 2 gal/A, and the second application was made in ~50 gal/A water without oil. Applications were made using ground equipment (tractor-mounted airblast sprayer). In the 1997 trials, peaches at separate plots at each trial site were harvested 14 and 28 days following a third application made to forming fruit at 0.25 lb ai/A (total seasonal application rate of 1 lb ai/A; 2x the maximum proposed seasonal rate). HED notes that the proposed use pattern prohibits application after petal fall. For the 3-application regimen, RTIs were 27-32 days between applications 1 and 2, and 64-134 days between

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applications 2 and 3. Applications at the Sultana, CA and Knightdale, NC sites were made in 82-100 gal/A water with dormant oil added to the first application spray at 8 and 2 gal/A, and applications at the Ripon, CA were made in 50-100 gal/A water with dormant oil added to the first application spray at 2 gal/A. An additional plot at each trial site was not treated for controls.

Peaches were hand-picked or harvested using a pole picker at maturity (78-158 days following the two-application regimen or 14 and 28 days following the three-application regimen). A single control and duplicate treated samples of ~7-15 lb each were collected from all trial sites, and were shipped to PTRL West, Inc. (Richmond, CA) for residue analysis.

Plums

Whole plums were collected at maturity following two applications of the 25% WP, 80% WDG, and/or 2 lb/gal FLC formulation made to dormant trees at ~0.50 lb ai/A and at petal fall at 0.25 lb ai/A, for a total seasonal application rate of 0.75 lb ai/A (1.5x the maximum proposed seasonal rate); RTIs were 22-49 days. The first and second applications were made in ~100 gal/A and ~50 gal/A water, with dormant oil added to the first application spray at 1.5-2 gal/A. Applications were made using ground equipment (tractor-mounted airblast sprayer). An additional plot at each trial site was not treated for controls.

Plums were hand-picked at maturity 104-196 days following the second application. A single control and duplicate treated samples were collected from all trial sites; sample weights were not provided, but the protocol specified that 7-lb samples should be collected. Plum samples were shipped to PTRL West, Inc. (Richmond, CA) for residue analysis.

7. Site Specific Information

Peaches

Cultural practices at selected sites included pruning, mowing, brush chopping, tilling, and/or disking between the trees; any fertilizers and/or maintenance chemicals used at the sites would not be expected to affect the residue data. At sites where trees were irrigated, peach trees received ~5-70" of irrigation. The petitioner reported that air temperature and precipitation were within the normal range vs. historical data for the field sites except as noted: lower temperatures in early May and higher temperatures in later May advanced fruit maturity at Knightdale, NC, resulting in over-ripe samples from the 28-day PHI; wetter conditions in May and June and drier than average conditions in July were observed at Barto, PA; 120-mph winds were reported 27 days after application two at Conklin, MI; hotter and drier conditions than normal were observed at Mustang, OK, resulting in smaller-than-usual fruits; precipitation above the 10-yr average occurred at Cochran, GA; and higher than normal temperatures and lower than normal precipitation occurred during May-July at Monetta, SC.

The petitioner indicated that weather data for most peach trials were not collected in compliance with GLP (i.e., weather instruments were not calibrated in according to GLP). Temperature minimums and maximums, and precipitation amounts were provided for each trial site; however, historical averages were not provided for comparison.

Plums

Cultural practices at selected sites included mowing and/or disking between the trees; any fertilizers and/or maintenance chemicals used at the sites would not be expected to affect the residue data. At sites where trees were irrigated, plum trees received irrigation 1 day/wk in May/June and 2 days/wk in July/August (Madera, CA) or a total of 15 inches (Ivanhoe, CA). The petitioner reported that air temperature and precipitation were within the normal range vs. historical data for the field sites except

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that precipitation was below normal at Conklin, MI, and conditions were wetter than normal during the bloom period and spring at Ivanhoe, CA, resulting in the plum harvest being delayed 3 weeks compared to the previous year.

The petitioner indicated that weather data for most plum trials were not collected in compliance with GLP (i.e., weather instruments were not calibrated in according to GLP). Temperature minimums and maximums, and precipitation amounts were provided for each trial site; however, historical averages were not provided for comparison.

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 EPA Barcode: D277691

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II. RESULTS

TABLE 1. Residue Data Summary from Crop Field Trials

Location (city, state)/ Year	Variety	Commodity/ Portion Analyzed	Formulation	Application					PHI (days)	Residues (mg/kg)				
				Single Rate (lbs ai/A)	No.	RTI (days) ¹	Total Rate (lbs ai/A) ²	Percent of Max Rate ³		DFB	CPU	PCA	Total	
Peaches														
Sultana, CA/ 1997 Region 10	Diamond Princess	Fruit	25% WP	0.52, 0.24, 0.24	3	27, 69	1	200	14	0.592, 0.600, 0.664	0.006, 0.007, 0.006	<0.005, <0.005, <0.005	<0.603, <0.612, <0.675	
									28	0.277, 0.277, 0.284	<0.005, <0.005, <0.005	<0.287, <0.287, <0.294		
				0.50, 0.25	2	20	0.75	150	97	0.009, 0.009, 0.009	<0.005, <0.005, <0.005	<0.019, <0.019, <0.019		
Ripon, CA/ 1997 Region 10	Starns	Fruit	25% WP	0.50, 0.26, 0.25	3	27, 134	1.01	202	14	0.147, 0.169, 0.204	<0.005, <0.005, <0.005	<0.005, <0.005, <0.005	<0.157, <0.179, <0.214	
									28	0.176, 0.150, 0.145	<0.005, <0.005, <0.005	<0.186, <0.160, <0.155		
				0.50, 0.25	2	27	0.75	150	148	0.010, 0.010, 0.012	<0.005, <0.005, <0.005	<0.020, <0.020, <0.022		

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Location (city, state)/ Year	Variety	Commodity/ Portion Analyzed	Formulation	Application				PHI (days)	Residues (mg/kg)			
				Single Rate (lbs ai/A)	No.	RTI (days) ¹	Total Rate (lbs ai/A) ²	Percent of Max Rate ³	DFB	CPU	PCA	Total
Knightdale, NC/ 1997 Region 2	Candor	Fruit	25% WP	0.50, 0.25, 0.25	3	32, 64	1	200	14	<0.005, <0.005, <0.005	<0.005, <0.005, <0.005	<0.221, <0.227, <0.233
									28	<0.005, 0.019, 0.160, 0.163	<0.005, <0.005, <0.005, <0.005	<0.169, <0.170, <0.173
									78	<0.005, 0.019, 0.020, 0.022	<0.005, <0.005, <0.005, <0.005	<0.029, <0.030, <0.032
Barto, PA/ 1998 Region 1	Redhaven	Fruit	25% WP	0.50, 0.25	2	22	0.75	150	96	<0.05, <0.05	<0.005, <0.005	<0.065, <0.065
Conklin, MI/ 1998 Region 5	Bellaire	Fruit	25% WP	0.50, 0.25	2	30	0.75	150	93	<0.05, <0.05	<0.005, <0.005	<0.065, <0.065
Escalon, CA/ 1998 Region 10	variety not available per petitioner	Fruit	25% WP	0.52, 0.25	2	40	0.77	154	158	<0.05, <0.05	<0.005, <0.005	<0.065, <0.065
			80% WDG						158	<0.05, <0.05	<0.005, <0.005	<0.065, <0.065
			2 lb/gal FIC						158	<0.05, <0.05	<0.005, <0.005	<0.065, <0.065
Mustang, OK/ 1998 Region 6	Redhaven	Fruit	25% WP	0.50, 0.25	2	40	0.75	150	97	<0.05, <0.05	<0.005, <0.005	<0.065, <0.065

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Location (city, state)/ Year	Variety	Commodity/ Portion Analyzed	Formulation	Application				PHI (days)	Residues (mg/kg)			
				Single Rate (lbs ai/A)	No.	R/T (days) ¹	Total Rate (lbs ai/A) ²	Percent of Max Rate ³	DFB	CPU	PCA	Total
Cochran, GA/ 1998 Region 2	Harvester	Fruit	25% WP	0.50, 0.25	2	19	0.75	150	<0.05, <0.05	<0.01, <0.01	<0.005, <0.005	<0.065, <0.065
			80% WDG	0.50, 0.25	2	19	0.75	150	<0.05, <0.05	<0.01, <0.01	<0.005, <0.005	<0.065, <0.065
			2 lb/gal FIC	0.50, 0.25	2	19	0.75	150	<0.05, <0.05	<0.01, <0.01	<0.005, <0.005	<0.065, <0.065
Monetta, SC/ 1998 Region 2	Contender	Fruit	25% WP	0.51, 0.25	2	39	0.76	152	<0.05, <0.05	<0.01, <0.01	<0.005, <0.005	<0.065, <0.065
Plums												
Conklin, MI/ 1998 Region 5	Stanley	Fruit	25% WP	0.50, 0.25	2	34	0.75	150	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.06, <0.06
Madera, CA/ 1998 Region 10	Autumn Butte	Fruit	25% WP	0.51, 0.26	2	28	0.77	154	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.06, <0.06
Sultana, CA/ 1998 Region 10	Angelos	Fruit	25% WP	0.51, 0.24	2	22	0.75	150	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.06, <0.06
Ivanhoe, CA/ 1998 Region 10	Simka	Fruit	2 lb/gal FIC	0.50, 0.26	2	49	0.76	152	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.06, <0.06
			80% WDG	0.50, 0.25	2	49	0.75	150	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.06, <0.06
			25% WP	0.50, 0.25	2	49	0.75	150	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.06, <0.06

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Location (city, state)/ Year	Variety	Commodity/ Portion Analyzed	Formulation	Application				PHI (days)	Residues (mg/kg)			
				Single Rate (lbs ai/A)	No.	RTI (days) ¹	Total Rate (lbs ai/A) ²	Percent of Max Rate ³	DFB	CPU	PCA	Total
Forest Grove, OR/ 1998 Region 12	Italian Prunes	Fruit	2 lb/gal F/C	0.49, 0.25	2	43	0.74	148	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.06, <0.06
			80% WDG	0.50, 0.25	2	43	0.75	150	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.06, <0.06
			25% WP	0.50, 0.25	2	43	0.75	150	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.06, <0.06

¹ RTI = retreatment interval (interval between applications).

² Actual application rates reported as rounded values (lb ai/A) by the petitioner were used to calculate total application rates.

³ Percent of maximum rate was calculated from the total rate applied (rounded value).

Apparent residues of diflubenzuron, CPU, and PCA were each nondetectable in/on five samples each of untreated plums. Apparent residues of diflubenzuron, CPU, and PCA were each nondetectable in/on 10, 6, and 10 samples, respectively, of untreated peaches from the 1998 trials. Apparent residues of diflubenzuron, CPU, and PCA were each nondetectable in/on six, four, and six samples, respectively, of untreated peaches from the 1997 trials; detectable residues of CPU (0.026 and 0.034 ppm) were observed in/on two untreated samples of peaches from the 1997 trials.

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Comments:

The available peach and plum field trial data indicate that residues of diflubenzuron and its metabolites CPU and PCA were each less than the method LOQs (<0.05 ppm for diflubenzuron, <0.01 ppm in peaches and <0.005 ppm in plums for CPU, and <0.005 ppm for PCA) in/on peaches from the 1998 trials and plums harvested 93-196 days following the last of two foliar applications of the 25% WP, 80% WDG, and/or 2 lb/gal FIC formulations made to dormant trees at 0.50 lb ai/A and at petal drop at 0.25 lb ai/A for a total of ~0.75 lb ai/A/application (1.5x the maximum proposed seasonal rate for stone fruits). Detectable residues of diflubenzuron at 0.009-0.022 ppm were reported in samples from the 1997 peach trials, in which the reported method LOQ for diflubenzuron was 0.005 ppm; residues of CPU and PCA were less than the LOQs (<0.005 each). Combined residues were <0.065 ppm in/on peaches from all trials and <0.060 ppm in/on plums. The mean residues were <0.065 ppm for peaches and <0.060 ppm for plums.

In peaches from the 1997 field trials harvested following a third application at 0.25 lb ai/A to forming fruit, combined residues of diflubenzuron, CPU, and PCA ranged <0.157-<0.675 ppm and <0.155-<0.294 ppm in/on peaches harvested 14 and 28 days, respectively, following the last of three foliar applications of the 25% WP formulation for a total of ~1.0 lb ai/A/application (2x the maximum proposed seasonal rate for stone fruits). These data are presented for informational purposes only; the proposed use pattern prohibits application after petal fall. HED notes that these data do demonstrate that residues generally declined from the 14-day PHI to the 28-day PHI.

Treated peach samples were stored for up to ~10, 14, and 12 months prior to analysis for residues of diflubenzuron, CPU, and PCA, respectively. Treated plum samples were stored for up to ~7, 11, and 10 months prior to analysis for residues of diflubenzuron, CPU, and PCA, respectively. Adequate storage stability data are available to support the storage conditions and intervals of samples from this study.

Adequate sample chromatograms were provided.

III. CONCLUSIONS

The results from supervised crop field trial studies (MRIDs 45252206-45252208) in peaches conducted in 1997 and 1998 in CA (3 trials), GA (1 trial), MI (1 trial), NC (1 trial), OK (1 trial), PA (1 trial), and SC (1 trial), and in plums conducted in 1998 in CA (3 trials), MI (1 trial), and OR (1 trial) indicate that the combined residues of diflubenzuron, and its metabolites CPU and PCA in/on peaches and plums collected 78-196 days following the last of two foliar applications made at dormancy and petal fall of the 25% WP, 80% WDG, and/or 2 lb/gal FIC formulations in side-by-side trials for a total seasonal application rate of ~0.75 lb ai/A (1.5x the maximum proposed seasonal rate for stone fruits), were less than the combined method LOQs (<0.065 ppm in/on peaches and <0.060 ppm in/on plums).

With respect to the side-by-side trials conducted with peaches and plums, because residues were below the method LOQs in all samples from the side-by-side trials, no differences were observed in residue levels following treatment with the 25% WP, the 80% WDG, or the 2 lb/gal FLC formulation.

Based on the available method validation conducted prior to analysis of field samples and concurrent recovery data, the methods (GC/ECD for diflubenzuron, GC/ECD or HPLC/MS for CPU, and GC/MS for PCA) used to quantitate residues of diflubenzuron, CPU, and PCA are adequate for data collection in/on peaches and plums. For residues of diflubenzuron, *per se*, the validated method LOQs were 0.005

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ppm for peaches from the 1997 trials and 0.05 ppm for peaches from the 1998 trials and plums. For residues of CPU, the validated method LOQs were 0.01 and 0.005 ppm for peaches from the 1998 trials and plums, respectively, analyzed by HPLC/MS, and 0.005 ppm for peaches from the 1997 trials analyzed by GC/ECD. For residues of PCA, the validated method LOQ was 0.005 ppm for PCA in/on peaches and plums. No interference was observed in representative chromatograms of control samples from the analysis of peaches and plums.

Because residues were below the LOQ in peaches and plums, the crop field trials for peaches and plums are classified as acceptable and satisfy the guideline requirement for crop field trials (Residue Chemistry Guidelines OPPTS 860.1500).

IV. STUDY DEFICIENCIES

No deficiencies were identified.

V. REFERENCES

DP Barcode: D209032
Subject: Diflubenzuron. Chemistry Chapter of the Reregistration Eligibility Document.
Reregistration Case No. 0144. Chemical No. 108201.
From: S. Knizner
To: S. Jennings and K. Whitby/L. Kutney
Date: 3/16/95
MRIDs: None

DP Barcode: D251484
Subject: PP#8F4925. Diflubenzuron (Dimilin® 2L, EPA Reg #400-461) on Rice. Request for
Petition Method Validation (PMV).
From: J. Rowell
To: D. Marlow
Date: 12/15/98
MRIDs: 44399303, 44399303, 44695001, and 44695002

DP Barcode: D253043, D253041, D244487, D251221, and D251609
Subject: PP#8F4925. Diflubenzuron (Dimilin® 2L, EPA Reg #400-461) on Rice. Amendments
of 8/19/98, 11/20/98, 12/3/98, 1/21/99, 1/27/99 & 2/3/99. Analytical Method for
Metabolites, Revised Label, Additional Residue, Storage Stability, and Rotational Crop
Data.
From: G. Kramer
To: M. Johnson/A. Sibold
Date: 2/17/99
MRIDs: 44577601, 44689701, 44689702, 44699201, 44692701, 44692703, 44695001, 44695002,
and 44707401

DP Barcode: D272978
Subject: PP#6E06167. Diflubenzuron (Dimilin® 2L, EPA Reg #400-461) in/on Pears.

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From: Evaluation of Residue Data and Analytical Methods.
To: G. Kramer
Date: S. Brothers/R. Forrest
4/3/01
MRIDs: 45119601 and 45119602

DP Barcode: D272976
Subject: Health Effects Division (HED Metabolism Assessment Review Committee (MARC)
Meetings of 2/20/01 & 5/8/01. Diflubenzuron. Residues of Concern for Cancer Risk
Assessment.

From: G. Kramer/G. Reddy
To: Y. Donovan
Date: 5/31/01
MRID: None

**DIFLUBENZURON
PC Code 108201
(DP Barcode D277691)**

**Processed Food/Feed, Plum;
OPPTS 860.1520**

January 30, 2002

Contract No. 68-W-99-053

**Submitted to:
U.S. Environmental Protection Agency
Arlington, VA**

**Submitted by:
Dynamac Corporation
20440 Century Boulevard, Suite 100
Germantown, MD 20874**

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MRID: 45252208
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EPA Reviewer: George F. Kramer, Ph.D., Date: 27-FEB-2002

STUDY TYPE: Processed Food/Feed Study - Plum; OPPTS 860.1520

TEST MATERIAL: Diflubenzuron (N-[[[(4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide); CPU (4-chlorophenylurea); and PCA (p-chloroaniline)

FORMULATION AND TYPE: Dimilin® 25W (25% wettable powder formulation; WP; EPA Reg. No. 400-465)

SYNONYMS: Diflubenzuron Tradenames: Dimilin, Vigilante, Micromite, Adept

CITATION: 45252208 Gaydos, K.A. (2001) Dimilin® 25W, Dimilin® 80WG, and Dimilin® 2 L in Plums and Prunes: Magnitude of the Residue Study. Study No.: RP-98002. Unpublished study submitted by Uniroyal Chemical Company, Inc. 370 p.

SPONSOR: Uniroyal Chemical Company, Inc.

EXECUTIVE SUMMARY:

In support of the proposed foliar use of diflubenzuron on stone fruit, Uniroyal has submitted a plum (prune) processing study (MRID 45252208). Detectable residues of diflubenzuron were observed at 0.136-0.187 ppm in/on plums collected 147 days following two foliar applications of the 25% WP formulation made at dormancy (2.0 lb ai/A) and at petal fall (1.0 lb ai/A) for a total application rate of 3.0 lb ai/A (6x the maximum proposed seasonal rate for stone fruits); residues of CPU and PCA were below the limit of quantitation (LOQ) (<0.005 ppm). The plums were processed into prunes according to simulated commercial procedures. Analysis indicated that residues of diflubenzuron reduced (0.8x) in prunes; therefore, a tolerance for residues of diflubenzuron in prunes is not required.

A Codex maximum residue limit (MRL) is established for residues of diflubenzuron in/on plums (including prunes) at 1 ppm. Mexican MRLs are established for residues of diflubenzuron per se; however, none is relevant to this petition. Use of diflubenzuron in Canada is limited to mosquito control; therefore, no Canadian MRLs have been established.

This processed food/feed study is classified acceptable and satisfies the guideline requirement for a processing study (Residue Chemistry Guidelines OPPTS 860.1520).

COMPLIANCE: Signed and dated GLP, Quality Assurance, and Data Confidentiality statements were provided. GLP deviations were reported concerning the test substance, weather, maintenance chemicals, and irrigation.

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I. MATERIALS AND METHODS

MATERIALS:

1. Test Compound:

Active ingredient (ai): Diflubenzuron

Formulation or spiking substance: 25% WP formulation

Physicochemical Properties (TGAI):

Water solubility (OPPTS 830.7840 and 830.7860)	Nearly insoluble in water (8×10^{-5} g/L) [PP#1F06235 Administrative Materials]
Organic solvent solubility (if available)	Soluble in organic solvents including n-hexane (0.063 g/L), toluene (0.29 g/L), dichloromethane (1.8 g/L), and methanol (1.1 g/L) at 20 C. [PP#1F06235 Administrative Materials]
n-Octanol/water partition coefficient (Kow) (OPPTS 830.7550)	$\log P = 3.89$ [PP#1F06235 Administrative Materials]
pKa (OPPTS 830.7370)	Not applicable because the TGAI is practically insoluble in water [PP#1F06235 Administrative Materials]
Vapor Pressure (OPPTS 830.7950)	9.3×10^{-10} mm Hg at 25 C [PP#1F06235 Administrative Materials]

2. Test Commodity:

Crop: Plum

Type/Variety: French Prune

Crop parts used in processing study: Whole fruit

Developmental stages (i.e., immature/mature, fresh/dry, etc.):

The first application was made during dormancy, just prior to bud swell, and the second application was made at petal fall; mature fruit was harvested.

Other: None

METHODS:

1. Experimental Design:

Method of application: Foliar broadcast spray

Rate of application (comparison to the maximum application rate): Total application rate of 3.0 lb ai/A, equivalent to 6x the maximum proposed seasonal application rate for stone fruits.

Application rate(s): First application: 2.0 lb ai/A; second application: 1.0 lb ai/A

Number of applications: 2

Number of test/control samples: Two samples each of untreated and treated mature plums weighing ~52 lb each.

Number of sample replicates: Duplicate treated and untreated samples were collected.

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2. Test Procedures:

Manner in which test compound was introduced into RAC (i.e., spiking, application):

In a single field trial conducted in CA in 1998, mature plums were harvested 147 days following the last of two foliar applications, made with a 26-day retreatment interval, of the 25% WP formulation at 2.0 and 1.0 lb ai/A/application for a total application rate of 3.0 lb ai/A/season (6x the maximum proposed seasonal rate for stone fruits). Applications were made using ground equipment (backpack mist blower). The first application was made at dormancy in 100 gal/A water with 2 gal/A of dormant oil, and the second application was made at petal fall in 50 gal/A water without oil.

Description of processing procedure and mass balance (include scheme if applicable):

Plums were processed into prunes using a commercial dryer; the processing procedure was initiated on the day of harvest at Sunsweet (Winters, CA). Plums were washed, placed in net bags, and dried on drying trays for ~18 hours. The petitioner noted that the drying trays were not washed prior to use and that the untreated and treated samples were placed on the same tray. Processed prune samples were stored frozen after processing. The processing procedure yielded 16- to 17-lb samples of prunes from each fresh plum sample.

Analytical methods:

Plum RAC and processed prune samples were analyzed for residues of diflubenzuron, CPU, and PCA using a GC/ECD (electron capture detection) method for diflubenzuron, an HPLC LC/MS method for CPU, and a GC/MS method for PCA. The petitioner reported that, due to extreme difficulties with matrix interferences, prunes were not analyzed for CPU. Samples were analyzed by PTRL West (Richmond, CA). The GC/ECD method used for the quantitation of diflubenzuron is similar to PAM Vol II, Method I; the GC method used for the quantitation of PCA is similar to that submitted previously for use on rice and its processed commodities and subsequently submitted for petition method validation (PMV) as an enforcement method (PP#8F4925, D251484, 12/15/98, J. Rowell). Brief descriptions of the methods follow.

Diflubenzuron - GC/ECD

Samples of plum and prunes (depitted) were analyzed for residues of diflubenzuron using a GC/ECD method entitled "Gas Chromatographic Determination of Diflubenzuron Residues in Apples Brussels Sprouts, and Artichokes." Samples were homogenized, then extracted with dichloromethane (2x) and vacuum filtered. The filtrates were combined, evaporated to dryness at ~35-45 C, and residues were redissolved in dichloromethane. Petroleum ether was added, and the solution was applied to a Florisil column for cleanup. Residues were eluted from the Florisil column with 20% acetone in petroleum ether, evaporated to dryness, and redissolved in 85% phosphoric acid. The acidic solution was heated at slow reflux for 30 minutes, cooled, and the hydrolysate was extracted with hexane. The aqueous phase was diluted with 50% NaOH in an ice bath to pH ≥ 12 . The resulting alkaline solution was extracted with hexane (3x). The hexane extracts were combined, and the volume was adjusted to 200 mL with additional hexane. Heptafluorobutyric anhydride (HFBA) was added to an aliquot of the hexane extract. After 10 minutes, water was added, and the organic phase was collected for analysis. Using this method, residues of diflubenzuron are converted to PCA and then derivatized with HFBA. The HFBA-derivatized PCA was

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quantitated by GC analysis using ECD; external calibration curves of diflubenzuron standards (HFBA-derivatized PCA) and peak area comparisons were utilized for quantitation. Residues were calculated as diflubenzuron using a molecular weight conversion factor. The reported method LOQ was 0.05 ppm for diflubenzuron in plums and prunes.

CPU - HPLC/MS

Samples of plums were analyzed for residues of CPU using an HPLC/MS method entitled "Dimilin 25W (Diflubenzuron): Non-food Aquatic Field Dissipation and Bioaccumulation in Aquatic Non-Target Organisms." Samples were homogenized and extracted with acetonitrile (ACN; 2x) and vacuum filtered or centrifuged. The filtrates/supernatants were combined, and the volume was adjusted with additional ACN. An aliquot was partitioned with hexane (2x), and the ACN phase was concentrated and partitioned twice again with hexane. The ACN phase was evaporated to dryness at ~40 C. Residues were redissolved in water and partitioned with ethyl acetate (2x). The ethyl acetate phases were combined, concentrated to dryness, and residues were redissolved in ACN and diluted with water to achieve a 1:4 ratio of ACN:water for cleanup through a C18 solid phase extraction (SPE) cartridge. Residues were eluted from the C18 SPE cartridge with ACN:water (1:1, v:v) and partitioned with hexane (2x). The ACN phase was evaporated to dryness, redissolved in diethyl ether:hexane (1:19, v:v), and applied to a silica SPE cartridge for further cleanup. Residues were eluted from the silica SPE cartridge with acetone:hexane (1:1, v:v) and evaporated to dryness. Residues were redissolved in ACN and diluted with water for HPLC analysis. CPU was quantitated by HPLC analysis using a Microsorb-C18 column, step gradient mobile phase of ACN and water, and mass spectrometry (MS) detection; external calibration curves of CPU standards and peak area comparisons were utilized for quantitation. The reported method LOQ was 0.005 ppm for CPU in plums. Prune samples were not analyzed for CPU because of difficulties with the method. HED will not require the analysis of prune samples for CPU because CPU residues were <LOQ in/on plum samples following treatment at 6x.

PCA - GC/MS

Samples of plums and prunes (depitted) were analyzed for residues of PCA using a GC/MS method with isotope dilution entitled "Method Validation for 4-Chloroaniline (PCA) at Low Levels Using 13-PCA as Internal Standard in Rice and Rice Commodities." Samples were homogenized, then mixed with solutions of ¹²C-PCA (fortified samples only) and ¹³C-PCA (internal standard). After 5 minutes, 0.1 N HCl was added, and the mixture was shaken at ~60 C in a water bath for 30 minutes. The cooled mixture was centrifuged, and the resulting supernatant was filtered. The pellet was further extracted with 0.1 N HCl (2x), shaken for 20 minutes, centrifuged, and filtered. The filtrates were combined, diluted with aqueous 50% NaOH to pH >12, then combined with solid NaCl. The solution was partitioned with hexane (3x) and centrifuged. The hexane phases were combined and partitioned with 0.1 N HCl (2x). Aqueous 50% NaOH was added to the combined acid phases until a pH ≥ 12 was achieved, and the extract was partitioned with hexane containing sodium sulfate (3x). The combined hexane phases were applied to a GRM florisil column for further cleanup. Residues were eluted from the Florisil column with 20% acetone in hexane, and HFBA was added to the eluate. After 10 minutes, water and saturated sodium carbonate were added, and the organic phase was collected for analysis. Using this method, residues of PCA are derivatized with HFBA. The HFBA-derivatized PCA was quantitated by GC/MS analysis

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with selective ion monitoring (SIM) of ions 323, 329, 126, and 132. Identification of PCA was by comparison of its retention time with the internal standard (^{13}C -PCA), and quantification was by integration of the peak area for ^{12}C -PCA relative to ^{13}C -PCA. In addition, comparison of the peak area of ^{12}C -PCA with the external standard linearity curve was used for quantitation (confirmation technique). Area ratio linearity curves were used to determine that the response was linear over the range of detection. The reported method LOQ was 0.005 ppm for PCA in plums and prunes

Method validation was performed on plums and processed prunes at the laboratory prior to analysis of the field trial samples. Recoveries of diflubenzuron ranged 79-89% (mean = $84 \pm 3\%$) in/on six untreated plum samples and 63-76% (mean = $71 \pm 6\%$) in six untreated prune samples fortified at 0.05 and 0.1 ppm. Recoveries of CPU ranged 96-124% (mean = $108 \pm 11\%$) in/on six untreated plum samples fortified with CPU at 0.005 and 0.01 ppm. Recoveries of PCA ranged 77-104% (mean = $93 \pm 9\%$) in/on six untreated plum samples and 99-117% (mean = $104 \pm 7\%$) in six untreated prune samples fortified at 0.005 and 0.010 ppm. Concurrent method recovery data (presented below under II. Table 1) were submitted. The validated method LOQs were 0.05 ppm for diflubenzuron, 0.005 ppm for CPU (plums only), and 0.005 ppm for PCA.

Storage stability:

Plums were harvested 147 days following the last foliar application, and the processing procedure was initiated on the day of harvest at Sunsweet (Winters, CA). Processing was completed the day after harvest, and processed prune samples were stored frozen and returned to the field facility. Frozen plum RAC and processed prune samples were shipped to PTRL West (Richmond, CA) for residue analysis within 22 days after processing. Samples were stored frozen (0 C) at the analytical laboratory prior to analysis. Total storage intervals from harvest to analysis were 172 and 198 days (~6-7 months) for diflubenzuron in/on plums and prunes, respectively; 291 days (<10 months) for CPU in/on plums; and 263 and 262 days (<9 months) for PCA in/on plums and prunes, respectively.

Previously submitted storage stability data have demonstrated residues of diflubenzuron to be stable in various RACs for up to 12 months storage (Diflubenzuron Reregistration Eligibility Decision Document, 3/16/95). PCA and CPU have been demonstrated to be unstable, degrading significantly after 1 and 3 months, respectively, in various RACs. Subsequent to the Diflubenzuron RED, storage stability data were submitted in conjunction with petitions for pears (PP#6E6167; D272978, 4/3/01, G. Kramer) and rice (PP#8F4925; DP Barcodes D253043, D253041, D244487, D251221, and D251609, 2/17/99, G. Kramer). These data indicate that residues of diflubenzuron *per se* were stable in/on pears for up to 2.5 months and in/on rice commodities (rice grain, straw, hulls, and bran) for up to 12 months; residues of CPU were relatively stable in/on rice commodities for up to 12 months, but decreased following 3 months storage in/on pears; and residues of PCA decreased significantly following 1 month storage in/on pears and rice commodities.

The available storage stability data support the storage intervals and conditions for residues of diflubenzuron in/on plum and prune samples from the processing study. Although the available storage stability data indicate that residues in field samples stored for >1 month for

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PCA and >3 months for CPU should be corrected for apparent decline during storage, correction for loss on storage would not significantly affect the results of this study because residues of residues of both metabolites in plums were below the LOQ (<0.005 ppm), significantly lower than the observed residues of diflubenzuron.

II. RESULTS

TABLE 1. Summary of Procedural Recoveries for Plum RAC and Processed Plums Spiked with Diflubenzuron, CPU, or PCA.

Analyte	Spiking Level (mg/kg)	Recoveries obtained (%)	Range (%)	Mean recovery (SD) ¹
Plums				
Diflubenzuron	0.10	87, 91	87-91	89
CPU	0.005	85, 138	85-138	112
PCA	0.005	104, 106	104-106	105
Prunes				
Diflubenzuron	0.10	69, 72	69-72	71
PCA	0.005	98, 99	98-99	99

¹ Standard deviation is not calculated for two points.

Comments:

The method validation and concurrent recovery data for plums and prunes indicate that the analytical methods used to quantitate residues of diflubenzuron, CPU, and PCA in the plum RAC and residues of diflubenzuron and PCA in prunes are adequate for data collection. The analytical method for the determination of CPU residues could not be validated for prune samples due to matrix interference; however, RAB1 concludes that no additional analysis attempts are required for this metabolite because residues of CPU were nondetectable in treated plum RAC samples, and residues of diflubenzuron and PCA did not concentrate in processed prune samples.

TABLE 2. Residue Levels of Diflubenzuron, CPU, and PCA in Plums and Processed Prunes.

Matrix/Fraction	Rate (lbs ai/A)	Total Residues (ppm) ¹			Processing factor ²
		DFB	CPU	PCA	
Plum RAC	3.0	0.136, 0.187 (0.162)	<0.005, <0.005	<0.005, <0.005	--
Prunes	3.0	0.116, 0.139 (0.128)	Not analyzed	<0.005, <0.005	0.8x

¹ Uncorrected residues are reported. Residues in prune samples processed from plum samples are listed respectively; average values are reported in parentheses.

² Processing factors were calculated by the study reviewer for diflubenzuron using average values.

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Apparent residues of diflubenzuron, CPU, and PCA were each nondetectable (<0.05, <0.005, and <0.005 ppm, respectively) in/on one untreated plum RAC sample; apparent residues of diflubenzuron and PCA were each nondetectable (<0.05 and <0.005 ppm, respectively) in/on one untreated prune sample.

Comments:

The exaggerated application rate produced quantifiable residues of diflubenzuron (0.136-0.187 ppm) in/on the plum RAC; residues of CPU and PCA were below the LOQ (<0.005 ppm). The processing data indicate that residues of diflubenzuron reduce in plums (0.8x) processed from plums bearing detectable diflubenzuron residue. The processing factor for prunes is less than the theoretical concentration factor of 3.5x.

TABLE 3. Processing Factors, Maximum Residues and Proposed Tolerances for Diflubenzuron in Plums and Processed Prunes.

RAC	Processed Commodity	Processing Factor	HAFT/Theoretical Max. Residue (ppm)	Proposed Tolerance (ppm)
		See Text		

Comments:

Because diflubenzuron residues were not found to concentrate in prunes, a tolerance for prunes is not required.

III. FINAL SUMMARY

The nature of the residue in plants is adequately understood. The MARC has determine the residues of concern in plant commodities are diflubenzuron and its metabolites CPU and PCA (DP Barcode D272976, 5/31/01, G. Kramer).

Detectable residues of diflubenzuron were observed at 0.136-0.187 ppm in/on plums collected 147 days following two foliar applications of the 25% WP formulation made at dormancy (2.0 lb ai/A) and at petal fall (1.0 lb ai/A) for a total application rate of 3.0 lb ai/A (6x the maximum proposed seasonal rate for stone fruits); residues of CPU and PCA were below the LOQ (<0.005 ppm). The plums were processed into prunes according to simulated commercial procedures. Analysis indicated that residues of diflubenzuron reduced (0.8x) in prunes; therefore, a tolerance for residues of diflubenzuron in prunes is not required.

A Codex MRL is established for residues of diflubenzuron in/on plums (including prunes) at 1 ppm. Mexican MRLs are established for residues of diflubenzuron per se; however, none is relevant to this petition. Use of diflubenzuron in Canada is limited to mosquito control; therefore, no Canadian MRLs have been established.

This processed food/feed study is classified acceptable and satisfies the guideline requirement for a processing study (Residue Chemistry Guidelines OPPTS 860.1520).

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IV. STUDY DEFICIENCIES

No deficiencies were identified.

V. REFERENCES

DP Barcode: D209032
Subject: Diflubenzuron. Chemistry Chapter of the Reregistration Eligibility Document.
Reregistration Case No. 0144. Chemical No. 108201.
From: S. Knizner
To: S. Jennings and K. Whitby/L. Kutney
Date: 3/16/95
MRIDs: None

DP Barcode: D251484
Subject: PP#8F4925. Diflubenzuron (Dimilin® 2L, EPA Reg #400-461) on Rice. Request for
Petition Method Validation (PMV).
From: J. Rowell
To: D. Marlow
Date: 12/15/98
MRIDs: 44399303, 44399303, 44695001, and 44695002

DP Barcode: D253043, D253041, D244487, D251221, and D251609
Subject: PP#8F4925. Diflubenzuron (Dimilin® 2L, EPA Reg #400-461) on Rice. Amendments
of 8/19/98, 11/20/98, 12/3/98, 1/21/99, 1/27/99 & 2/3/99. Analytical Method for
Metabolites, Revised Label, Additional Residue, Storage Stability, and Rotational Crop
Data.
From: G. Kramer
To: M. Johnson/A. Sibold
Date: 2/17/99
MRIDs: 44577601, 44689701, 44689702, 44699201, 44692701, 44692703, 44695001, 44695002,
and 44707401

DP Barcode: D272978
Subject: PP#6E06167. Diflubenzuron (Dimilin® 2L, EPA Reg #400-461) in/on Pears.
Evaluation of Residue Data and Analytical Methods.
From: G. Kramer
To: S. Brothers/R. Forrest
Date: 4/3/01
MRIDs: 45119601 and 45119602

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DP Barcode: D272976

Subject: Health Effects Division (HED Metabolism Assessment Review Committee (MARC)
Meetings of 2/20/01 & 5/8/01. Diflubenzuron. Residues of Concern for Cancer Risk
Assessment.

From: G. Kramer/G. Reddy

To: Y. Donovan

Date: 5/31/01

MRIDs: None

DIFLUBENZURON
PC Code 108201
(DP Barcode D277691)

Crop Field Trials, Peppers;
OPPTS 860.1500

January 30, 2002

Contract No. 68-W-99-053

Submitted to:
U.S. Environmental Protection Agency
Arlington, VA

Submitted by:
Dynamac Corporation
20440 Century Boulevard, Suite 100
Germantown, MD 20874

Chemical Name Diflubenzuron
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Crop Field Trials
GL: OPPTS 860.1500
PP#1F06235

MRID: 45252211
Case No.: 293515
Submission: S602900

EPA Reviewer: George F. Kramer, Ph.D., Date: 27-FEB-2002

STUDY TYPE: Crop Field Trials - Peppers; OPPTS 860.1500

TEST MATERIAL: Diflubenzuron (N-[[[(4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide); CPU (4-chlorophenylurea); and PCA (p-chloroaniline)

FORMULATION AND TYPE: Dimilin® 25% wettable powder (WP) formulation (EPA Reg. No. 400-465)

SYNONYMS: Diflubenzuron Tradenames: Dimilin, Vigilante, Micromite, Adept

CITATION: 45252211 Gaydosh, K.A.; Puhl, J.F. (2001) Dimilin® 25W on Bell and Non-Bell Peppers: Magnitude of the Residue Study. Study No.: RP-97016. Unpublished study submitted by Uniroyal Chemical Company, Inc. 1115 p.

SPONSOR: Uniroyal Chemical Company, Inc.

EXECUTIVE SUMMARY:

In support of the proposed foliar use of diflubenzuron on peppers, Uniroyal has submitted the results from supervised crop field trials (MRID 45252211) on bell peppers conducted in CA (2 trials), FL (1 trial), IN (1 trial), NC (1 trial), and TX (1 trial) and on non-bell peppers conducted in CA (1 trial), NM (1 trial), and TX (1 trial). The combined residues of diflubenzuron and its metabolites CPU and PCA were <0.065-<0.281 ppm in/on bell peppers and <0.229-<0.997 ppm in/on non-bell peppers harvested 7 days following the last of five foliar applications of the 25% WP formulation at 0.125 lb ai/A/application for a total seasonal application rate of ~0.625 lb ai/A (1x the maximum proposed seasonal rate for peppers).

Based on the available method validation conducted prior to analysis of field samples and concurrent recovery data, the three GC methods used to quantitate residues of diflubenzuron, CPU, and PCA are adequate for data collection in/on peppers (bell and non-bell). The validated method limit of quantitation (LOQ) was 0.05 ppm for diflubenzuron, 0.01 ppm for CPU, and 0.005 ppm for PCA in peppers; no interference was observed in representative chromatograms of control samples from the analysis of peppers.

No residue decline data were submitted. HED generally requires residue decline data when a pesticide is applied when the edible portion of the crop has formed and/or it is clear that quantifiable residues may occur on food or feed commodities at the earliest harvest time. However, decline data were submitted with the stone fruit residue trials (45252206.der.wpd). These data do demonstrate that residues generally declined from the 14-day PHI to the 28-day PHI. HED is willing to translate these data to peppers and concludes that additional residue decline data on peppers will not be required.

The crop field trials for peppers are classified acceptable and satisfy the guideline requirement for crop field trials (Residue Chemistry Guidelines OPPTS 860.1500).

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COMPLIANCE: Signed and dated GLP, Quality Assurance and Data Confidentiality statements were provided. GLP deviations were reported concerning inspection and equipment SOPs, QA auditors, signature dates, and cultural practices.

I. MATERIALS AND METHODS

Pepper samples were analyzed for residues of diflubenzuron, CPU and PCA using GC/ECD methods for diflubenzuron and CPU, and a GC/MS method for PCA. Samples were analyzed by PTRL West (Richmond, CA). The GC/ECD method used for the quantitation of diflubenzuron is similar to PAM Vol II, Method I; the GC methods used for the quantitation of CPU and PCA are similar to those submitted previously for use on rice and subsequently submitted for petition method validation (PMV) as enforcement methods (PP#8F4925, D251484, 12/15/98, J. Rowell). Brief descriptions of the methods follow.

Diflubenzuron - GC/ECD

Samples of peppers were analyzed for residues of diflubenzuron using a GC/ECD method entitled "Method Validation for Diflubenzuron in Rice Grain, Rice Straw, Hulls, and Bran." Samples were homogenized and extracted with dichloromethane and vacuum filtered. The filtrate was evaporated to dryness at -35 C, and residues were redissolved in dichloromethane. Petroleum ether was added, and the solution was applied to a Florisil column for cleanup. Residues were eluted from the Florisil column with 20% acetone in petroleum ether, evaporated to dryness, and redissolved in 85% phosphoric acid. The acidic solution was heated at slow reflux for 30 minutes, cooled, and the hydrolysate was extracted with hexane. The aqueous phase was diluted with 50% NaOH in an ice bath to pH \geq 12. The resulting alkaline solution was extracted with hexane (3x). Hexane extracts were combined, and the volume was adjusted to 200 mL with additional hexane. Heptafluorobutyric anhydride (HFBA) was added to an aliquot of the hexane extract. After 10 minutes, water was added, and the organic phase collected for analysis. Using this method, residues of diflubenzuron are converted to PCA, which is then derivatized with HFBA. The HFBA-derivatized PCA was quantitated by GC analysis using electron capture detection (ECD); external calibration curves of diflubenzuron standards (HFBA-derivatized PCA) and peak area comparisons were utilized for quantitation. Residues were calculated as diflubenzuron using a molecular weight conversion factor. The reported method LOQ was 0.05 ppm for diflubenzuron in peppers.

CPU - GC/ECD

Samples of peppers were analyzed for residues of CPU using a GC/ECD method entitled "Dimilin 25@ on Raw and Processed Rice and Processed Rice, Processing Study at 8x Rate." Samples were homogenized and extracted with ethyl acetate, then vacuum filtered. The filtrate was evaporated to dryness at -35 C, and residues were redissolved in acetone. Petroleum ether was added, and the solution was applied to a deactivated silica gel column for cleanup. Residues were eluted from the silica column with ethanol:petroleum ether (30:70, v:v), evaporated to dryness, redissolved in hexane, evaporated to dryness again, and redissolved in acetonitrile (ACN). HFBA was added to a small aliquot of the ACN-suspended residues. After 10 minutes, water, saturated sodium carbonate, and hexane were added, and the organic phase was collected for analysis. Using this method, residues of CPU are derivatized with HFBA. The HFBA-derivatized CPU was quantitated by GC analysis using ECD detection; external calibration curves of HFBA-derivatized CPU standards and peak area comparisons were utilized for quantitation. The reported method LOQ was 0.01 ppm for CPU in peppers.

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PCA - GC/MS

Samples of peppers were analyzed for residues of PCA using a method entitled "Method Validation for 4-Chloroaniline (PCA) at Low Levels Using ^{13}C -PCA as Internal Standard in Rice and Rice Commodities." Samples were homogenized, then mixed with solutions of ^{12}C -PCA (fortified samples only) and ^{13}C -PCA (internal standard). After 5 minutes 0.1 N HCl was added, and the mixture was shaken at ~60 C in a water bath for 30 minutes. The cooled mixture was centrifuged, and the resulting supernatant was filtered. The pellet was further extracted with 0.1 N HCl (2x), then shaken for 20 minutes, centrifuged, and filtered. The filtrates were combined, diluted with aqueous 50% NaOH to pH >12, then combined with solid NaCl. The solution was partitioned with hexane (3x) and centrifuged. The hexane phases were combined and partitioned with 0.1 N HCl (2x). Aqueous 50% NaOH was added to the combined acid phases until a pH \geq 12 was achieved, and the extract was partitioned with hexane containing sodium sulfate (3x). The combined hexane phases were applied to a GRM Florisil column for further cleanup. Residues were eluted from the Florisil column with 20% acetone in hexane, and HFBA was added to the eluate. After 10 minutes, water and saturated sodium carbonate were added, and the organic phase was collected for analysis. Using this method, residues of PCA are derivatized with HFBA. The HFBA-derivatized PCA was quantitated by GC/MS analysis with selective ion monitoring (SIM) of ions 323, 329, 126, and 132. Identification of PCA was by comparison of its retention time with the internal standard (^{13}C -PCA), and quantification was by integration of the peak area for ^{12}C -PCA relative to ^{13}C -PCA. In addition, comparison of the peak area of ^{12}C -PCA with the external standard linearity curve was used for quantitation (confirmation technique). Area ratio linearity curves were used to determine that the response was linear over the range of detection. The reported method LOQ was 0.005 ppm for PCA in peppers.

Method validation was performed at the laboratory prior to analysis of the field trial samples. Recoveries of diflubenzuron ranged 66-104% (mean = $87 \pm 9\%$) in/on 18 untreated pepper samples fortified at 0.05-1.00 ppm. Recoveries of CPU ranged 76-110% (mean = $91 \pm 11\%$) in/on 18 untreated pepper samples fortified at 0.01-0.60 ppm. Recoveries of PCA were 80-117% (mean = $99 \pm 8\%$) in/on 18 untreated pepper samples fortified at 0.005-0.050 ppm. Concurrent method recovery data (presented below under 1.4.) were submitted; the validated method LOQs were 0.05 ppm for diflubenzuron, 0.01 ppm for CPU, and 0.005 ppm for PCA in peppers.

Sample chromatograms of control and treated samples were provided; no interference was observed in the regions of diflubenzuron, CPU, or PCA in chromatograms for control samples of peppers.

1. Test Compound

Chemical name

IUPAC: 1-(4-Chlorophenyl)-3-(2,6-difluorobenzoyl)urea

CAS name: Benzamide, -[[[(4-chlorophenyl)amino]carbonyl]-2,6-difluoro-

CAS #: 35367-38-5

Common name (ANSI, BSI or ISO): Diflubenzuron

Developmental (Company) name: Not available

Chemical name

IUPAC: 4-Chlorophenyl urea

CAS name: Not available

CAS #: 140-38-5

Common name (ANSI, BSI or ISO): CPU

Developmental (Company) name: Not applicable (metabolite)

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Chemical name

IUPAC: p-Chloroaniline or 4-chloroaniline

CAS name: Benzenamine, 4-chloro

CAS #: 106-47-8

Common name (ANSI, BSI or ISO): PCA

Developmental (Company) name: Not applicable (metabolite)

2. Trial Numbers and Locations

Crop Peppers	US Growing Regions						Total Trials
	2	3	5	6	8	10	
Submitted - Bell peppers	1	1	1	1	--	2	6
Requested - Bell peppers ¹	1	1	1	1	--	2	6
Submitted - Non-Bell peppers	--	--	--	1	1	1	3
Requested - Non-bell peppers ¹	--	--	--	--	--	--	3

¹ OPPTS 860.1500, Tables 4 and 5. Requested number of trials for bell peppers represents a 25% reduction in the number of trials because bell and non-bell peppers constitute a "general category" under 40 CFR 180.1(h). OPPTS 860.1500 Table 5 does not identify specific regions for non-bell pepper field trials.

Comments:

Geographic representation reflecting the proposed use pattern for diflubenzuron on peppers is adequate. As required under OPPTS GLN 860.1500 (Tables 4 and 5) six trials were conducted for bell peppers in Regions 2 (1 trial), 3 (1 trial), 5 (1 trial), 6 (1 trial), and 10 (2 trials), and three trials were conducted for non-bell peppers in Regions 6, 8, and 10, which together account for ~70% of non-bell pepper production (OPPTS 860.1500, Table 6).

3. Proposed Label Use Pattern

80% WDG (Dimilin® 80WG; EPA File Symbol No. 400-XXX)

2 lb/gal FIC (Dimilin® 2L; EPA Reg. No. 400-461)

Crop	Application					Comments/ Restrictions
	Method/ Timing	Maximum Single Application Rate	Maximum Number of Applications	Total Seasonal Rate	PHI (days)	
Pepper	Foliar	0.125 lb ai/A	5	0.625 lb ai/A (implied)	7	A minimum retreatment interval (RTI) of 7 days is specified. Applications are to be made using ground equipment in a minimum of 30 gal/A water. Adjuvants or oil (1 pint to 2 quarts/A) may be added.

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The use pattern presented above is from specimen labels included in the administrative materials for PP#1F06235. The petitioner indicated that the 80% WDG formulation is identical to an 80% WDG formulation (Micromite® 80WG; EPA Reg. No. 400-487) that is currently registered for use on citrus in Florida only. We note that specimen labels included in MRID 45252209 for the 25% WP formulation (Dimilin® 25W; EPA Reg. No. 400-465) and the 80% WDG formulation did not include use directions for peppers.

The proposed use directions for the 80% WDG formulation (EPA File Symbol No. 400-XXX) and the 2 lb/gal FIC formulation (EPA File Symbol No. 400-461) are adequate to allow HED an assessment of whether the submitted residue data reflect the maximum residues likely to occur in peppers. Use directions were not provided for the 25% WP formulation.

The petitioner must submit a revised Section B including use directions for the 25% WP formulation if the petitioner intends it to be used on peppers. In addition, because the test substance was formulated with water only for all applications to peppers, the submitted field trial data will not support the use of adjuvants or oil; the use directions for the addition of adjuvants or oil at 1 pint to 2 quarts/A must be removed.

4. Analytical Method Validation (Concurrent)

Peppers; Analyte	Spiking Level (mg/kg)	Recoveries obtained (%)	Range (%)	Mean recovery (SD)
Diflubenzuron	0.2	82, 93, 98, 105, 113, 118, 119, 120, 125, 133	82-133	111 (16)
CPU	0.2	70, 74, 76, 84, 105, 118, 118, 122, 122, 132	70-132	102 (24)
PCA	0.005	69, 86, 93, 94, 96, 103	69-103	90 (12)

Comments:

Based on the available method validation conducted prior to analysis of field samples and concurrent recovery data, the three GC methods used to quantitate residues of diflubenzuron, CPU, and PCA are adequate for data collection in/on peppers (bell and non-bell).

5. Storage Stability Conditions

Commodity	Storage Temperature (°C)	Duration (days)		
		DFB	CPU	PCA
Peppers (bell and non-bell)	Not specified	172-340	178-357	177-347

Comments:

Pepper samples were frozen at the field site within 4 hours of harvest and were shipped frozen within 119 days of harvest to PTRL West (Richmond, CA) for residue analysis. Samples were stored frozen at the laboratory until sample preparation. Treated samples were analyzed within 8 days of extraction. Treated pepper samples were stored for up to 340, 357, and 347 days (<12 months) prior to analysis for diflubenzuron, CPU, and PCA, respectively.

A storage stability study was conducted concurrently with the field trial studies; refer to 45252211.de2.wpd for details and results of the study. The storage stability data indicate that residues of

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diflubenzuron *per se* and CPU are relatively stable in/on bell peppers stored frozen for up to 12 months. However, although CPU recoveries were within the acceptable range, some level of decline of CPU residues was observed (~20%) following 3 months of frozen storage. PCA recoveries in fortified bell pepper samples decreased significantly (~30%) following 1 month frozen storage and decreased ~70% following 12 months frozen storage. Because residues of PCA degraded significantly after 1 month, field samples stored for >1 month for PCA should be corrected in order to determine the residue levels that were present at the time of sample collection. Residues of diflubenzuron in/on peppers were 1-4 orders of magnitude greater than that of PCU and CPU in/on treated crop samples; therefore, HED has determined that correction of PCA residues for degradation during storage would not have a significant effect on the results of the field trial studies. These data are adequate to support the storage conditions and intervals of the field trial samples.

6. Application and RAC Information

Bell and non-bell peppers were harvested 7 days following the last of five applications at 7-day retreatment intervals of the 25% WP formulation at ~0.125 lb ai/A/application, for a total seasonal application rate of 0.625 lb ai/A (1x the maximum proposed seasonal rate). Applications were made in ~30 ga/A using ground equipment (backpack, tractor-mounted or self-propelled CO₂ sprayer or bicycle-mounted compressed air sprayer). An additional plot at each trial site was not treated for controls.

A single control and duplicate treated samples of ~4-12 lb were hand-picked from each trial site and were shipped to PTRL West, Inc. (Richmond, CA) for residue analysis.

7. Site-Specific Information

Cultural practices at selected sites included cultivation or hand weeding; any fertilizers and/or maintenance chemicals used at the sites would not be expected to affect the residue data. Irrigation, ranging from 1-6" was reported at all sites except the Florida site. The petitioner reported that air temperature and precipitation were within the normal range vs. historical data for the field sites except as noted: slightly cooler temperatures and higher precipitation in June and lower precipitation in July at Lodi, CA; high temperatures and low precipitation in June and July at Knightdale, NC affected fruit development (80% of full size at harvest); low precipitation in September and high precipitation in October at Donna, TX; and cooler temperatures and higher precipitation April-June, and hotter temperatures and low precipitation in July at East Bernard, TX.

The petitioner indicated that weather data for most pepper trials were not collected in compliance with GLP (i.e., weather instruments were not calibrated in according to GLP). Temperature minimums and maximums, and precipitation amounts were provided for each trial site; however, historical averages were not provided for comparison.

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II. RESULTS

TABLE 1. Residue Data Summary from Crop Field Trials

Location (city, state)/ Year	Variety	Commodity/ Portion Analyzed	Formulation	Application				PHI, days	Residues (mg/kg) ⁴			
				Single Rate (lbs ai/A)	No.	RTI (days) ¹	Total Rate (lbs ai/A) ²		Percent of Max Rate ³	DFB	CPU	PCA
Bell Pepper												
Lodi, CA/ 1997 Region 10	Bombay	Fruit	25% WP	0.125	5	7	0.625	100	0.229, 0.253	<0.010, <0.010	<0.005, <0.005	<0.244, <0.268
Noblesville, IN/ 1997 Region 5	California Wonder	Fruit	25% WP	0.125-0.131	5	7	0.631	101	0.208, 0.262	0.013, 0.014	<0.005, <0.005	<0.226, <0.281
Knightdale, NC/ 1997 Region 2	Yolo Wonder	Fruit	25% WP	0.125	5	7	0.625	100	0.050, 0.093	0.010, <0.010	<0.005, <0.005	<0.065, <0.108
San Marcos, CA/ 1997 Region 10	Jupiter	Fruit	25% WP	0.106-0.131	5	7	0.613	98	<0.050, 0.098	<0.010, 0.038	<0.005, <0.005	<0.065, <0.141
Immokalee, FL/ 1997 Region 3	California Wonder	Fruit	25% WP	0.125	5	7	0.625	100	<0.050, 0.125	<0.010, <0.010	<0.005, <0.005	<0.065, <0.140
Donna, TX/ 1997 Region 6	Jupiter	Fruit	25% WP	0.125-0.131	5	7	0.631	101	0.326, 0.328	0.057, 0.027	<0.005, <0.005	<0.388, <0.360
Non-Bell Pepper												
East Bernard, TX/ 1997 Region 6	Anaheim	Fruit	25% WP	0.125	5	7	0.625	100	0.896, 0.935	<0.010, 0.057	<0.005, <0.005	<0.911, <0.997
Rincon, NM/ 1997 Region 8	Anaheim	Fruit	25% WP	0.125-0.131	5	7	0.631	101	0.916, 0.950	<0.010, <0.010	<0.005, <0.005	<0.931, <0.965
San Marcos, CA/ 1997 Region 10	Anaheim 23 TMR	Fruit	25% WP	0.119-0.125	5	7	0.613	98	0.214, 0.289	<0.010, <0.010	<0.005, <0.005	<0.229, <0.304

¹ RTI = retreatment interval (interval between applications).

² Actual application rates reported as rounded values (oz ai/A) by the petitioner were used to calculate individual and total application rates.

³ Percent of maximum rate was calculated from the total rate applied (rounded value).

⁴ **Bolded** residues reflect the proposed use pattern.

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Apparent residues of diflubenzuron, CPU, and PCA were each nondetectable (<0.05, <0.01, and <0.005 ppm, respectively) in/on six samples of untreated bell peppers and three samples of untreated non-bell peppers.

Comments:

The submitted pepper field trial data indicate that residues ranged <0.050-0.262 ppm for diflubenzuron, <0.010 (LOQ)-0.038 ppm for CPU, and <0.005 ppm (LOQ) for PCA in/on bell peppers and 0.214-0.950 ppm for diflubenzuron, <0.010 (LOQ)-0.057 ppm for CPU, and <0.005 ppm (LOQ) for PCA in/on non-bell peppers. Combined residues were <0.065-<0.281 ppm in/on bell peppers and <0.229-<0.997 ppm in/on non-bell peppers harvested 7 days following the last of five foliar applications at 7-day RTIs of the 25% WP formulation at 0.125 lb ai/A/application, for a total seasonal rate of ~0.625 lb ai/A/application (1x the maximum proposed seasonal rate for peppers). For the combined residues of diflubenzuron, CPU, and PCA, the mean residue is 0.372 ppm for peppers.

Data were only submitted for the WP formulation. HED has determined that WP and WDG formulations are sufficiently similar to allow translation of residue data between them; however, additional data are required to support use of the 2 lb/gal FIC formulation on peppers.

Treated pepper samples were stored for up to 357 days (<12 months). A storage stability study was conducted concurrent with the field trial studies; refer to D277691 DER 860.1380 for details and results of the study. The storage stability data indicate that residues of diflubenzuron *per se* and CPU are relatively stable in bell peppers stored frozen for up to 12 months. However, although CPU recoveries were within the acceptable range, some level of decline of CPU residues was observed (~20%) following 3 months of frozen storage. PCA recoveries in fortified bell pepper samples decreased significantly (~30%) following 1 month frozen storage and decreased ~70% following 12 months frozen storage. Because residues of PCA degraded significantly after 1 month, field samples stored for >1 month for PCA, should be corrected in order to determine the residue levels that were present at the time of sample collection. Residues of diflubenzuron in/on peppers were 1-4 orders of magnitude greater than that of PCU and CPU in/on treated crop samples; therefore, HED has determined that correction of PCA residues for degradation during storage would not have a significant effect on the results of the field trial studies. These data are adequate to support the storage conditions and intervals of the field trial samples.

Sample chromatograms of control and treated samples were provided; no interference was observed in the regions of diflubenzuron, CPU, and PCA in chromatograms for control samples of peppers.

III. CONCLUSIONS

The results from supervised crop field trials (MRID 45252211) on bell peppers conducted in CA (2 trials), FL (1 trial), IN (1 trial), NC (1 trial), and TX (1 trial) and on non-bell peppers conducted in CA (1 trial), NM (1 trial), and TX (1 trial) indicate that the combined residues of diflubenzuron and its metabolites CPU and PCA were <0.065-<0.281 ppm in/on bell peppers and <0.229-<0.997 ppm in/on non-bell peppers harvested 7 days following the last of five foliar applications of the 25% WP formulation at 0.125 lb ai/A/application for a total seasonal application rate of ~0.625 lb ai/A (1x the maximum proposed seasonal rate for peppers).

Based on the available method validation conducted prior to analysis of field samples and concurrent recovery data, the three GC methods used to quantitate residues of diflubenzuron, CPU, and PCA are

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adequate for data collection in/on peppers (bell and non-bell). The validated method LOQ was 0.05 ppm for diflubenzuron, 0.01 ppm for CPU, and 0.005 ppm for PCA in peppers; no interference was observed in representative chromatograms of control samples from the analysis of peppers.

No residue decline data were submitted. HED generally requires residue decline data when a pesticide is applied when the edible portion of the crop has formed and/or it is clear that quantifiable residues may occur on food or feed commodities at the earliest harvest time. However, decline data were submitted with the stone fruit residue trials (45252206.der.wpd). These data do demonstrate that residues generally declined from the 14-day PHI to the 28-day PHI. HED is willing to translate these data to peppers and concludes that additional residue decline data on peppers will not be required.

The crop field trials for peppers are classified acceptable and satisfy the guideline requirement for crop field trials (Residue Chemistry Guidelines OPPTS 860.1500).

IV. STUDY DEFICIENCIES

A single residue decline study is required for peppers to demonstrate that residues do not increase with longer PHIs. The residue decline study may be incorporated into the outstanding field trials. The proposed PHI can not be assessed until residue decline data are available.

At least two side-by-side field trials must be conducted with the 2 lb/gal FIC and the 25% WP formulation to demonstrate that residues in/on peppers are not significantly different between the different formulations. The side-by-side studies may include the outstanding decline trial. The proposed use for the 2 lb/gal FIC cannot be registered until the bridging data are available.

V. REFERENCES

DP Barcode: D251484
Subject: PP#8F4925. Diflubenzuron (Dimilin® 2L, EPA Reg #400-461) on Rice. Request for Petition Method Validation (PMV).
From: J. Rowell
To: D. Marlow
Date: 12/15/98
MRIDs: 44399303, 44399306, 44695001, and 44695002

DP Barcode: D272976
Subject: Health Effects Division (HED Metabolism Assessment Review Committee (MARC) Meetings of 2/20/01 & 5/8/01. Diflubenzuron. Residues of Concern for Cancer Risk Assessment.
From: G. Kramer/G. Reddy
To: Y. Donovan
Date: 5/31/01
MRID: None

**DIFLUBENZURON
PC Code 108201
(DP Barcode D277691)**

**Crop Field Trials, Tree Nuts;
OPPTS 860.1500**

January 30, 2002

Contract No. 68-W-99-053

**Submitted to:
U.S. Environmental Protection Agency
Arlington, VA**

**Submitted by:
Dynamac Corporation
20440 Century Boulevard, Suite 100
Germantown, MD 20874**

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EPA Reviewer: George F. Kramer, Ph.D., Date: 27-FEB-2002

STUDY TYPE: Crop Field Trials - Tree Nuts; OPPTS 860.1500

TEST MATERIAL: Diflubenzuron (N-[[[(4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide);
CPU (4-chlorophenylurea); and PCA (p-chloroaniline)

FORMULATION AND TYPE: Dimilin® 25W (25% wettable power formulation; WP; EPA Reg.
No. 400-465); Dimilin® 2L (2 lb/gal flowable concentrate
formulation; FIC; EPA Reg. No. 400-461); and Dimilin® 80 WG
(80% water dispersible granular formulation; WDG; EPA File
Symbol No. 400-XXX)

SYNONYMS: Diflubenzuron Tradenames: Dimilin, Vigilante, Micromite, Adept

CITATION: 45252209 Gaydosh, K.A. (2000) Dimilin® 25W, Dimilin® 80WG, and Dimilin® 2L in
Almonds: Magnitude of the Residue Study. Study No.: RP-98003. Unpublished study
submitted by Uniroyal Chemical Company, Inc. 469 p.

45252210 Gaydosh, K.A. (2000) Dimilin® 2L, Dimilin® 80WG, and Dimilin® 25W in
Pecans: Magnitude of the Residue Study. Study No.: RP-99002. Unpublished study
submitted by Uniroyal Chemical Company, Inc. 384 p.

SPONSOR: Uniroyal Chemical Company, Inc.

EXECUTIVE SUMMARY:

In support of the proposed foliar use of diflubenzuron on tree nuts including pistachios, Uniroyal Chemical Company has submitted the results from supervised crop field trial studies (MRIDs 45252209 and 45252210) with almonds conducted in CA (5 trials) and pecans conducted in GA (2 trials), LA (1), NM (1), and OK (1). Samples of almond and pecan nutmeats and hulls were collected 27-28 days following the last of four foliar applications of diflubenzuron at 0.5 lb ai/A/application (applications 1 and 4) and 0.25 lb ai/A/application (applications 2 and 3) for a total seasonal application rate of ~1.5 lb ai/A (1.5x the maximum proposed seasonal rate for tree nuts). For the almond field trials, side-by-side trials were conducted at one field site using the 25% WP formulation, the 2 lb/gal FIC formulation, and the 80% WDG formulation; the 25% WP formulation alone was used at the remaining field sites. For the pecan field trials, side-by-side trials using all three formulations were conducted at one GA site and the LA and OK sites, and the 2 lb/gal FIC formulation alone was used at the remaining GA site and the NM site. Combined residues of diflubenzuron and its metabolites CPU and PCA were less than the combined method limits of quantitation (LOQ) (<0.060 ppm) in/on almond and pecan nutmeats and <0.987-<5.547 in/on almond hulls.

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With respect to the side-by-side trials conducted in almonds and pecans, no significant differences were observed in residue levels in almond or pecan hulls following treatment with the 25% WP, the 80% WDG, or the 2 lb/gal FIC formulation in the side-by-side trials. Residues were <2.883 and <3.651 ppm, <3.409 and <5.547 ppm, and <2.921 and <3.140 ppm, respectively, in/on almond hulls following treatment with the 25% WP, the 80% WDG, and the 2 lb/gal FIC formulations. Residues were <0.080-0.771 ppm (n=6), <0.065-<0.381 ppm (n = 6), and <0.113-<1.392 ppm (n = 10), respectively, in/on pecan hulls (discussed here for informational purposes only) following treatment with the 25% WP, the 80% WDG, and the 2 lb/gal FIC formulations.

Based on the available method validation and concurrent recovery data, the analytical methods (HPLC for diflubenzuron and CPU, and GC for PCA) used to quantitate residues of diflubenzuron, CPU, and PCA are adequate for data collection in/on almond and pecan nutmeats and hulls. The validated method LOQs were <0.05 ppm for diflubenzuron in/on nutmeats and hulls, <0.005 and <0.010 ppm for CPU in/on nutmeats and hulls, respectively, and <0.005 ppm for PCA in/on nutmeats and hulls. No interference was observed in representative chromatograms of control samples from the analysis of almond and pecan nutmeats and hulls.

The trials were conducted at 1.5x the maximum proposed application rate. However, the final application of the test substance (typically the application that determines the residues in the crop at harvest) was made at the maximum per application rate. Because the *per application rate was 1x*, the crop field trials for tree nuts are classified as acceptable. The data satisfy the guideline requirement for crop field trials (Residue Chemistry Guidelines OPPTS 860.1500) for tree nuts. Based on the results of these trials, the petitioner should propose a tolerance of 6.0 ppm for the combined residues of diflubenzuron, CPU, and PCA in/on "almond, hulls."

The petitioner did not submit residue decline data; however, because the preharvest interval (PHI) is fairly long (28 days), HED will not require a decline study in this case. PMRA does not require residue decline studies for PHIs >14 days.

COMPLIANCE: Signed and dated GLP, Quality Assurance, and Data Confidentiality statements were provided. For some trials, handling of the test substance, collection of weather data, and/or generation/maintenance of test site records including application of maintenance chemicals and irrigation were not conducted in compliance with GLP Standards.

I. MATERIALS AND METHODS

Almond and pecan samples were analyzed for residues of diflubenzuron, CPU, and PCA using an HPLC/UV method for diflubenzuron, an HPLC method with UV or MS detection for CPU, and a GC/MS method with isotope dilution for PCA. Samples were analyzed by PTRL West (Richmond, CA). The GC method used for the quantitation of PCA is similar to that submitted previously for use on rice and subsequently submitted for petition method validation (PMV) as an enforcement method (PP#8F4925, D251484, 12/15/98, J. Rowell). Brief descriptions of the methods follow.

Diflubenzuron

Samples of almond and pecan nutmeats and hulls were analyzed for residues of diflubenzuron using an HPLC/UV method entitled "High Performance Liquid Chromatographic Determination of Diflubenzuron

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Residues in Pecan Nuts.” Samples were homogenized, then extracted with ethyl acetate (2x) and vacuum filtered. The filtrates were combined, evaporated to dryness, and residues were redissolved in hexane and extracted with acetonitrile (ACN). The ACN extract was partitioned with hexane (2x), evaporated to dryness, and the residues were redissolved in dichloromethane. Petroleum ether was added, and the solution was applied to a Florisil column for cleanup. Residues were eluted from the Florisil column with acetone:petroleum ether (1:4, v:v). The eluate was evaporated to dryness and redissolved in 1,4-dioxane. The dioxane solution was diluted with ACN:water (1:1, v:v) for HPLC analysis. Diflubenzuron was quantitated by HPLC analysis using a Zorbax XDB-C8 column, step gradient mobile phase of ACN, water, and 1,4-dioxane, and UV (254 nm) detection; external calibration curves of diflubenzuron standards and peak area comparison were utilized for quantitation. The reported method LOQ was 0.05 ppm for diflubenzuron in nutmeats and hulls.

CPU

Samples of almond and pecan nutmeats and hulls were analyzed for residues of CPU using an HPLC method with MS or UV detection entitled “Dimilin 25W (Diflubenzuron): Non-food Aquatic Field Dissipation and Bioaccumulation in Aquatic Non-Target Organisms.” HED notes that the GC method originally proposed for analysis of CPU was replaced with this method due to problems related to fats in almonds and pecans. Samples were homogenized, then extracted with ACN (2x) and centrifuged (almonds) or vacuum filtered (pecans). The supernatants or filtrates were combined and adjusted to volume with additional ACN. An aliquot was partitioned with hexane (2x), and the ACN phase was concentrated and partitioned with hexane (2x), then evaporated to dryness at ~40 C. Residues were reconstituted in ACN and diluted with water to achieve a 1:4 ratio of ACN:water for cleanup through a C18 solid phase extraction (SPE) cartridge. Residues were eluted from the C18 cartridge with ACN:water (1:1, v:v), and the eluate was partitioned with hexane (2x). The ACN phase was evaporated to dryness, redissolved in diethyl ether:hexane (1:19, v:v), and applied to a silica SPE cartridge for further cleanup. Residues were eluted from the silica SPE cartridge with acetone:hexane (1:1, v:v), and the eluate was evaporated to dryness. CPU residues in almond samples were reconstituted in ACN and diluted with water for HPLC analysis. CPU residues in pecans were redissolved in hexane for further cleanup through an amino SPE cartridge. Residues were eluted from the amino SPE cartridge with acetone, evaporated to dryness, and redissolved in ACN:water (1:1, v:v) for HPLC analysis. CPU is quantitated by HPLC analysis using a Microsorb C18 column and a step gradient mobile phase of ACN and water. Almond samples were analyzed using mass spectrometry (MS) detection. One set of pecan samples were analyzed using MS detection, but because of matrix suppression of the MS ionization, the remaining samples were analyzed using UV (254 nm) detection; external calibration curves of CPU standards and peak area comparison were utilized for quantitation. The reported LOQs were 0.005 ppm and 0.010 ppm for CPU in nutmeats and hulls, respectively.

PCA

Samples of almond and pecan nutmeats and hulls were analyzed for residues of PCA using a GC/MS method with isotope dilution entitled “Method Validation for 4-Chloroaniline (PCA) at Low Levels Using ¹³C-PCA as Internal Standard in Rice and Rice Commodities.” Samples were homogenized, then mixed with solutions of ¹²C-PCA (fortified samples only) and ¹³C-PCA (internal standard). After 5 minutes, 0.1 N HCl was added, and the mixture was shaken at ~60 C in a water bath for 30 minutes. The cooled mixture was centrifuged, and the resulting supernatant was filtered. The pellet was further extracted with 0.1 N HCl (2x), shaken for 20 minutes, centrifuged, and filtered. The filtrates were

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combined, diluted with aqueous 50% NaOH to pH >12, then combined with solid NaCl. The solution was partitioned with hexane (3x) and centrifuged. The hexane phases were combined and partitioned with 0.1 N HCl (2x). Aqueous 50% NaOH was added to the combined acid phases until a pH \geq 12 was achieved, and the extract was partitioned with hexane containing sodium sulfate (3x). The combined hexane phases were applied to a GRM Florisil column for further cleanup. Residues were eluted from the Florisil column with 20% acetone in hexane, and heptafluorobutyric anhydride (HFBA) was added to the eluate. After 10 minutes, water and saturated sodium carbonate were added, and the organic phase was collected for analysis. Using this method, residues of PCA are derivatized with HFBA. The HFBA-derivatized PCA was quantitated by GC/MS analysis with selective ion monitoring (SIM) of ions 323, 329, 126, and 132 or 154, 323, 160, and 329. Identification of PCA was by comparison of its retention time with the internal standard (^{13}C -PCA), and quantification was by integration of the peak area for ^{12}C -PCA relative to ^{13}C -PCA. In addition, comparison of the peak area of ^{12}C -PCA with the external standard linearity curve was used for quantitation (confirmation technique). Area ratio linearity curves were used to determine that the response was linear over the range of detection. The reported method LOQ was 0.005 ppm for PCA in nutmeats and hulls.

Method validation (MRID 45252209) was performed on almond nutmeats and hulls at the laboratory prior to analysis of the field trial samples; recoveries ranged 70-85% (mean = $80 \pm 5\%$) in/on eight samples of untreated almond nutmeat and 70-93% (mean = $81 \pm 7\%$) in/on nine samples of untreated almond hull samples fortified with diflubenzuron at 0.05-0.5 ppm; recoveries ranged 84-97% (mean = $92 \pm 6\%$) in/on six samples of untreated almond nutmeat fortified with CPU at 0.005-0.010 ppm and 85-110% (mean = $98 \pm 12\%$) in/on three samples of untreated almond hull samples fortified with CPU at 0.010 ppm; and recoveries ranged 69-98% (mean = $82 \pm 11\%$) in/on six samples of untreated almond nutmeat and 82-102% (mean = $94 \pm 9\%$) in/on six samples of untreated almond hull fortified with PCA at 0.005-0.010 ppm. Concurrent method recovery data (presented below under I.4.) were submitted; the validated method LOQs were 0.05 ppm for diflubenzuron in/on nutmeats and hulls, 0.005 ppm and 0.010 ppm for CPU in/on nutmeats and hulls, respectively, and 0.005 ppm for PCA in/on nutmeats and hulls. HED notes that the petitioner included method validation data reflecting poor recoveries in samples fortified at levels below the "validated" LOQ; however, these data are not presented herein.

Sample chromatograms of control and treated samples were provided; no interference was observed in the regions of diflubenzuron, CPU, or PCA in chromatograms for control samples of nutmeats and hulls.

1. Test Compound

Chemical name

IUPAC: 1-(4-Chlorophenyl)-3-(2,6-difluorobenzoyl)urea

CAS name: Benzamide, N-[[[4-chlorophenyl]amino]carbonyl]-2,6-difluoro-

CAS #: 35367-38-5

Common name (ANSI, BSI or ISO): Diflubenzuron

Developmental (Company) name: Not available

Chemical name

IUPAC: 4-Chlorophenyl urea

CAS name: Not available

CAS #: 140-38-5

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Common name (ANSI, BSI or ISO): CPU
Developmental (Company) name: Not applicable (metabolite)

Chemical name

IUPAC: p-Chloroaniline or 4-chloroaniline

CAS name: Benzenamine, 4-chloro

CAS #: 106-47-8

Common name (ANSI, BSI or ISO): PCA

Developmental (Company) name: Not applicable (metabolite)

2. Trial Numbers and Locations

Crop Tree Nuts	US Growing Regions						Total Trials
	2	4	6	8	9	10	
Submitted - Almonds ¹	--	--	--	--	--	5	5
Requested - Almonds ²	--	--	--	--	--	5	5
Submitted - Pecans	2 ³	1 ³	1 ³	--	1	--	5
Requested - Pecans ²	2	1	1	1	--	--	5

¹ One trial included three separate treatment plots: one each for the 25% WP formulation, the 2 lb ai/gal FIC formulation, and the 80% WDG formulation; at the remaining trial sites only the 25% WP formulation was used.

² OPPTS 860.1500, Table 5. Requested number of trials represents a 25% reduction in the number of trials for a representative commodity used to obtain a crop group tolerance.

³ One trial in Region 2 and the trials in Regions 4 and 6 included three separate treatment plots: one each for the 25% WP formulation, the 2 lb ai/gal FIC formulation, and the 80% WDG formulation; at the remaining trial sites, only the 2 lb ai/gal FIC formulation was used.

Comments:

Geographic representation reflecting 1.5x the proposed use pattern is adequate for the tree nut crop group. As required under OPPTS GLN 860.1500 (Tables 2 and 5) for the representative crops of the tree nut crop group, five trials each were conducted for almonds and pecans. Almond field trials were conducted in Region 10 as required. Pecan field trials were conducted in Regions 2 (2 trials), 4 (1 trial), and 6 (1 trial) as required, and in Region 9 (1 trial). Although the fifth pecan trial was conducted in Region 9 instead of Region 8, the location of the field site was near the border for Region 8 and is thus acceptable. Because HED has concluded that pistachios are to be included as a member of the tree nuts crop group and that field residue data for almonds will be translatable to pistachios, geographic representation is adequate for pistachios as well.

3. Proposed Label Use Pattern

80% WDG (Dimilin® 80WG; EPA File Symbol No. 400-XXX)

2 lb/gal FIC (Dimilin® 2L; EPA Reg. No. 400-461)

Chemical Name **Diffubenzuron**
PC Code: **108201**
EPA Barcode: **D277691**

Crop Field Trials
GL: **OPPTS 860.1500**
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Crop	Application					Comments/ Restrictions
	Method/ Timing	Maximum Single Application Rate	Maximum Number of Applications	Total Seasonal Rate	PHI (days)	
Tree Nuts ¹	Foliar	0.25 lb ai/A	4 (3 walnuts)	1 lb ai/A	28	A minimum retreatment interval (RTI) of 21 days is specified. Applications are to be made in a minimum of 50 gal/A water for small trees (≤ 10 feet tall) or 100 gal/A for larger trees using ground equipment. Oil (maximum of 8 gal/A for dormant stage applications or 1 quart/A for other stage applications) may be added.

¹ Specific tree nuts listed on the label were almond, beech nut, brazil nut, butternut, cashew, chestnut, chinquapin, filbert (hazelnut), hickory nut, macadamia nut (bush nut), pecan, walnut (black and English), and pistachios.

The use pattern presented above is from specimen labels included in the administrative materials for PP#1F06235. The petitioner indicated that the 80% WDG formulation is identical to an 80% WDG formulation (Micromite® 80WG; EPA Reg. No. 400-487) that is currently registered for use on citrus in Florida only. HED notes that specimen labels included in MRID 45252209 for the 25% WP formulation (Dimilin® 25W; EPA Reg. No. 400-465) and the 80% WDG formulation did not include use directions for tree nuts.

The proposed use directions for the 80% WDG formulation (EPA File Symbol No. 400-XXX) and the 2 lb/gal FIC formulation (EPA File Symbol No. 400-461) are adequate to allow HED an assessment of whether the submitted residue data reflect the maximum residues likely to occur in tree nuts. Use directions for tree nuts were not provided for the 25% WP formulation.

The petitioner must submit a revised Section B to reflect the application timing represented in the field trials. The 2 lb/gal FIC and 80% WDG labels must be amended to specify RTIs and/or growth stages at which individual applications are to be made. In both studies, applications were made when trees were dormant to pre-bud swell (application 1), at bloom to petal fall (application 2), at flowers/leaves/immature nuts (application 3) and at hull split (application 4). RTIs were ~21 days between applications 1 and 2; 72-83 days between applications 2 and 3 for almonds and 21-28 days for pecans; and 70-175 days between applications 3 and 4. In addition, because the test substance was formulated with water only for applications 2-4, the submitted field trial data will not support the addition of oil to the tank mix for any applications other than the initial dormant stage application; therefore, the directions for the addition of 1 quart/A of oil for other stage applications must be removed on tree nuts.

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4. Analytical Method Validation (Concurrent)

Analyte	Spiking Level (mg/kg)	Recoveries obtained (%)	Range (%)	Mean recovery (SD)
Almond nutmeat				
Diflubenzuron	0.05, 0.10	80, 81, 84, 84, 98, 99	80-99	88 (9)
CPU	0.005	101, 102, 102, 118, 119, 129	101-129	112 (12)
PCA	0.005	101, 101, 106, 111, 113, 117	101-117	108 (7)
Almond hulls				
Diflubenzuron	0.05-2.5	85, 92, 93, 98, 111, 114	85-114	99 (11)
CPU	0.01	80, 83, 86, 89, 115, 130	80-130	97 (20)
PCA	0.005	94, 98, 103, 108, 110, 111	94-111	104 (7)
Pecan nutmeat				
Diflubenzuron	0.05-0.5	70, 70, 76, 78, 79, 79, 80, 81, 81, 82	70-82	78 (4)
CPU	0.005, 0.010	69, 70, 75, 76, 77, 82, 83, 90	69-90	78 (7)
PCA	0.005	97, 97, 97, 99, 99, 102, 109, 110, 112, 120	97-120	104 (8)
Pecan hulls				
Diflubenzuron	0.05-2.0	70, 70, 78, 79, 81, 82, 84, 85, 85, 94	70-94	81 (7)
CPU	0.01	74, 74, 75, 76, 78, 80, 82, 83	74-83	78 (4)
PCA	0.005	75, 79, 79, 93, 95, 96, 96, 104	75-104	90 (10)

Comments:

Based on the available method validation and concurrent recovery data, the three methods (HPLC for diflubenzuron and CPU, and GC for PCA) used to quantitate residues of diflubenzuron, CPU, and PCA are adequate for data collection in/on almond and pecan nutmeats and hulls.

5. Storage Stability Conditions

Commodity	Storage Temperature (°C)	Duration (days)		
		DFB	CPU	PCA
Almond nutmeat	Frozen (temp. not specified)	66-151	269-292	90-138
Almond hulls	Frozen (temp. not specified)	77-116	293-312	128-148
Pecan nutmeat	Frozen (temp. not specified)	43-92	149-193	119-178
Pecan hulls	Frozen (temp. not specified)	43-79	175-195	154-173

Comments:

Whole almonds were allowed to air-dry on the ground for up to 5 days in some trials and were stored at ambient temperatures until shipment to the processing laboratory (Plant Sciences, Manteca, CA), where

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they were stored at ambient temperatures prior to processing into nutmeat and hulls; whole almonds were stored at ambient conditions for up to 20 days. The petitioner noted that almonds were stored at ambient conditions prior to processing because frozen or thawed almonds cannot be hulled successfully. At the processing laboratory, samples from three of the trials were subjected to additional air-drying (up to 6 days) at the processing laboratory prior to separation of the nutmeat and hulls using a small-scale almond processor. Once almond nutmeats and hulls were separated, samples were stored frozen and were shipped frozen to PTRL West, Inc. (Richmond, CA) for residue analysis. Treated almond samples were stored for up to 151, 312, and 148 days (~5, 10.5, and 5 months) prior to analysis for residues of diflubenzuron, CPU, and PCA, respectively.

Whole pecans were separated into nutmeats and hulls either mechanically or by hand and were placed in freezers at the field sites within 87 hours of harvest. Samples were shipped frozen by ACDS freezer truck within 29 days of harvest to PTRL West (Richmond, CA) for residue analysis, where they were stored frozen until sample preparation. Treated samples were analyzed within 20 days of extraction. Treated pecan samples were stored for up to 92, 195, and 178 days (~3, 6.5, and 6 months) prior to analysis for residues of diflubenzuron, CPU, and PCA, respectively.

Previously submitted storage stability data have demonstrated residues of diflubenzuron to be stable in various raw agricultural commodities (RACs) for up to 12 months storage (Diflubenzuron Reregistration Eligibility Decision Document (RED), 3/16/95). PCA and CPU have been demonstrated to be unstable, degrading significantly after 1 and 3 months, respectively, in various RACs. Subsequent to the Diflubenzuron RED, storage stability data were submitted in conjunction with a petition for pears (PP#6E6167; D272978, 4/3/01, G. Kramer) and rice (PP#8F4925; DP Barcodes D253043, D253041, D244487, D251221, and D251609, 2/17/99, G. Kramer). These data indicate that residues of diflubenzuron *per se* were stable in/on pears for up to 2.5 months and in/on rice commodities (rice grain, straw, hulls, and bran) for up to 12 months; residues of CPU were relatively stable in/on rice commodities for up to 12 months, but decreased following 3 months storage in/on pears; and residues of PCA decreased significantly following 1 month storage in/on pears and rice commodities.

In addition, data from a storage stability study that was conducted concurrently with the pepper field trial studies submitted with the subject petition (PP#1F06235; 45252211.de2.wpd) indicate that residues of diflubenzuron *per se* and CPU are relatively stable in bell peppers stored frozen for up to 12 months. Although CPU recoveries were within the acceptable range, some decline in CPU residues was observed (~20%) following 3 months of frozen storage. PCA recoveries in fortified bell pepper samples decreased significantly (~30%) following 1 month frozen storage and decreased ~70% following 12 months frozen storage.

The available storage stability data support the storage intervals and conditions for residues of diflubenzuron in/on almond and pecan samples from the field trials. Although the available storage stability data indicate that residues in field samples stored for >1 month for PCA and >3 months for CPU should be corrected for apparent decline during storage, correction for loss on storage would not significantly affect the results of the almond or pecan field trial studies because residues of diflubenzuron in/on almond hulls were several orders of magnitude greater than those of PCA, which were near or below the LOQ (<0.005-0.0083 ppm), and CPU, which were less than the LOQ (<0.010 ppm), and

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because residues of both metabolites in almond and pecan nutmeats were below the LOQ of 0.005 ppm, which is an order of magnitude lower than the LOQ of 0.05 ppm for diflubenzuron.

6. Application and RAC Information

Almonds

Mature almonds at five field sites in CA were harvested 28 days following the last of four applications of the 25% WP formulation at ~0.50 lb ai/A (first and fourth applications) and 0.25 lb ai/A (second and third applications), for a total seasonal application rate of 1.5 lb ai/A, except at the Ripon, CA site, where the first two applications were made at 0.79 lb ai/A and 0.37 lb ai/A due to a miscalculation in the plot size, resulting in a total seasonal application rate of 1.83 lb ai/A for that trial. At the Reedley, CA site, almonds in separate plots were also treated with the 2 lb/gal FIC formulation and the 80% WDG formulation according to the same use pattern. Applications were made when trees were dormant to pre-bud swell (application 1), at bloom to petal fall (application 2), when immature nuts had formed (application 3) and at immature nuts to hull split (application 4). RTIs were 21-25 days between applications 1 and 2; 72-83 days between applications 2 and 3; and 70-175-days between applications 3 and 4. The first application was made in ~100-145 GPA water with dormant oil added at 2-6 gal/A; applications 2-4 were made in ~49-74 GPA water without oil. Applications were made using ground equipment (tractor-mounted airblast sprayer). An additional plot at each trial site was not treated for controls.

Whole almonds were harvested by shaking or knocking them off the trees. Almonds from two trials were allowed to dry on the ground for up to five days. All almonds were then raked for sample collection. A single control and duplicate treated samples of ~100 lb each were collected from all trial sites. Whole almonds were shipped to the processing laboratory (Plant Sciences, Manteca, CA), for separation into nutmeats and hulls using a small-scale almond processor. Nutmeats and hulls were then shipped to PTRL West, Inc. (Richmond, CA) for residue analysis.

Pecans

Mature pecans at field sites in GA (2 trials), LA, NM, and OK were harvested 27-28 days following the last of four applications of the 2 lb/gal FIC formulation (all trials), and the 80% WDG and 25% WP formulations (LA, OK, and Finleyson, GA trials) at ~0.50 lb ai/A (first and fourth applications) and 0.25 lb ai/A (second and third applications), for a total seasonal application rate of ~1.5 lb ai/A. Applications were made when trees were dormant to pre-bud swell (application 1), at early leaf/blooming to post bloom (application 2), when flowers/leaves had formed to early fruit set (application 3) and at ore-shuck split to shuck split (application 4). RTIs were 21-28 days between applications 1 and 2; 14-28 days between applications 2 and 3; and 150-175 days between applications 3 and 4. The first application was made in 99-102 GPA water with dormant oil added at 1.5-2 gal/A (except NM site); applications 2-4 were made in 48-52 GPA water without oil. Applications were made using ground equipment (tractor-mounted airblast sprayer). An additional plot at each trial site was not treated for controls.

Whole pecans were harvested by shaking them off the trees. Pecans from the two GA trials were harvested 27 days after the fourth application and were collected the following day; pecans from the remaining trials were collected on the day they were removed from the trees. A single control and duplicate treated samples of whole pecans weighing >5 lb each were collected from all trial sites except

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the OK site, where samples of whole pecans were not weighed before they were separated into samples of nutmeats and hulls weighing ~1.1-1.5 lb each. Pecans were separated into nutmeats and hulls by hand or by mechanical sheller at the field sites before they were placed in frozen storage. Nutmeats and hulls were then shipped to PTRL West, Inc. (Richmond, CA) for residue analysis.

7. Site-Specific Information

Almonds

Cultural practices at all sites were limited to mowing between the trees; any fertilizers and/or maintenance chemicals used at the sites would not be expected to affect the residue data. Almond trees received 16-36" of irrigation, and the petitioner reported that air temperature and precipitation were within the normal range vs. historical data for all sites except the Reedley, CA site, where it was noted that higher precipitation and lower temperatures during the bloom period and spring may have delayed almond maturity by ~3 weeks. Control samples from this site were reported to be immature by the processor.

The petitioner indicated that weather data for most almond and pecan trials were not collected in compliance with GLP (i.e., weather instruments were not calibrated in according to GLP). Temperature minimums and maximums, and precipitation amounts were provided for each trial site; however, historical averages were not provided for comparison.

Pecans

Normal cultural practices were implemented at the field sites; any fertilizers and/or maintenance chemicals used at the sites would not be expected to affect the residue data. Pecan trees received irrigation at one GA site (trickle irrigation at ~0.2 inches/day), the OK site (~192 gal/tree/wk), and the NM site (1-2x/mo. for a total of 67.5 inches). The petitioner reported that air temperature and precipitation were within the normal range vs. historical data except as follows: (i) precipitation was below average in April-June, August, October, and November, and above average in July, and temperatures were above average in August at the Finleyson, GA site; (ii) precipitation was below average in April, May, and August, and temperatures were above average in April, August, and November at the Eastman, GA site; (iii) precipitation was significantly below average for most of the study at the LA site; and (iv) weather was described as "hot and dry" at the OK site.

The petitioner indicated that weather data for most of the almond and pecan trials were not collected in compliance with GLP (i.e., weather instruments were not calibrated in according to GLP). Temperature minimums and maximums, and precipitation amounts were provided for each trial site; however, historical averages were not provided for comparison.

II. RESULTS

TABLE 1. Residue Data Summary from Crop Field Trials

Location (city, state)/ Year	Variety	Commodity/ Portion Analyzed	Formulation	Application					PHI (days)	Residues (mg/kg)				
				Single Rate (lbs ai/A)	No.	RTI (days)	Total Rate (lbs ai/A)	Percent of Max Rate		DFB	CPU	PCA	Total	
Almonds														
Madera, CA/ 1998 Region 10	Nonpareil	Nutmeat	25% WP	0.50 0.25 0.25 0.50	4	21, 81, 86	1.5	150	28	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.060, <0.060	
		Hull		2.132, 2.112						<0.010, <0.010	<0.005, 0.0083	<2.147, <2.130		
Kerman, CA/ 1998 Region 10	Nonpareil	Nutmeat	25% WP	0.51 0.24 0.26 0.50	4	25, 72, 70	1.51	151	28	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.060, <0.060	
		Hull		2.264, 2.272						<0.010, <0.010	<0.005, <0.005	<2.279, <2.287		
Reedley, CA/ 1998 Region 10	Butte	Nutmeat	25% WP	0.50 0.25 0.25 0.50	4	21, 79, 83	1.5	150	28	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.060, <0.060	
		Hull		3.636, 2.868						<0.010, <0.010	<0.005, <0.005	<3.651, <2.883		
		Nutmeat	2 lb/gal FIC	0.50 0.25 0.25 0.50	4	21, 79, 83	1.5	150	28	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.060, <0.060	
		Hull		3.125, 2.904						<0.010, <0.010	<0.005, 0.0067	<3.140, <2.921		
		Nutmeat	80% W/DG	0.51 0.25 0.25 0.50	4	21, 79, 83	1.51	151	28	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.060, <0.060	
		Hull		5.532, 3.392						<0.010, <0.010	0.0052, 0.0074	<5.547, <3.409		

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Location (city, state)/ Year	Variety	Commodity/ Portion Analyzed	Formulation	Application					PHI (days)	Residues (mg/kg)					
				Single Rate (lbs ai/A)	No.	RTI (days)	Total Rate (lbs ai/A)	Percent of Max Rate		DFB	CPU	PCA	Total		
Manteca, CA/ 1998 Region 10	Nonpareil	Nutmeat	25% WP	0.50 0.25 0.25 0.50	4	21, 78, 89	1.5	150	28	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.060, <0.060		
		Hull		<0.987, 1.079							<0.010, <0.010	<0.005, <0.005	<1.094		
Ripon, CA/ 1998 Region 10	Nonpareil	Nutmeat	25% WP	0.72 0.37 0.25 0.50	4	21, 83, 114	1.83	183	28	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.060, <0.060		
		Hull		1.469, 1.608							<0.010, <0.010	<0.005, <0.005	<1.484, <1.623		
Pecans															
Finleyson, GA/ 1999 Region 2	Stuarts	Nutmeat	2 lb/gal FIC	0.50 0.25 0.25 0.50	4	21, 21, 154	1.5	150	27	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.060, <0.060		
		Hulls		0.522, 0.643							<0.010, <0.010	<0.005, <0.005	<0.537, <0.658		
		Nutmeat	80% WDG	0.50 0.25 0.25 0.50	4	21, 21, 154	1.5	150	27	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.060, <0.060		
		Hulls		0.311, 0.366							<0.010, <0.010	<0.005, <0.005	<0.326, <0.381		
				Nutmeat	25% WP	0.50 0.25 0.25 0.50	4	21, 21, 154	1.5	150	27	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.060, <0.060
				Hulls		0.209, 0.231							<0.010, <0.010	<0.005, <0.005	<0.224, <0.246
Eastman, GA/ 1999 Region 2	Desirable	Nutmeat	2 lb/gal FIC	0.51 0.25 0.25 0.49	4	21, 14, 150	1.5	150	27	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.060, <0.060		
	Hulls	0.891, 1.377		<0.010, <0.010							<0.005, <0.005	<0.906, <1.392			

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Location (city, state)/ Year	Variety	Commodity/ Portion Analyzed	Formulation	Application					PHI (days)	Residues (mg/kg)			
				Single Rate (lbs ai/A)	No.	RTJ (days)	Total Rate (lbs ai/A)	Percent of Max Rate		DFB	CPU	PCA	Total
Opelousas, LA/ 1999 Region 4	Melrose	Nutmeat	2 lb/gal FIC	0.50	4	21, 24, 157	1.5	150	28	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.060, <0.060
		Hulls		0.25 0.25 0.50						0.334, 0.402	<0.010, <0.010	<0.005, <0.005	<0.349, <0.417
		Nutmeat	80% WDG	0.50	4	21, 24, 157	1.5	150	28	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.060, <0.060
		Hulls		0.25 0.25 0.50						0.203, 0.331	<0.010, <0.010	<0.005, <0.005	<0.218, <0.346
		Nutmeat	25% WP	0.50	4	21, 24, 157	1.5	150	28	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.060, <0.060
		Hulls		0.25 0.25 0.50						0.368, 0.756	<0.010, <0.010	<0.005, <0.005	<0.383, <0.771
Duncan, OK/ 1999 Region 6	Natives	Nutmeat	2 lb/gal FIC	0.50	4	28, 22, 152	1.51	151	28	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.060, <0.060
		Hulls		0.25 0.26 0.50						0.098, 0.182	<0.010, <0.010	<0.005, <0.005	<0.113, <0.197
		Nutmeat	80% WDG	0.50	4	28, 22, 152	1.51	151	28	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.060, <0.060
		Hulls		0.25 0.25 0.50						<0.05, <0.05	<0.010, <0.010	<0.005, <0.005	<0.065, <0.065
		Nutmeat	25% WP	0.50	4	28, 22, 152	1.5	150	28	<0.05, <0.05	<0.005, <0.005	<0.005, <0.005	<0.060, <0.060
		Hulls		0.25 0.26 0.50						0.065, 0.090	<0.010, <0.010	<0.005, <0.005	<0.080, <0.105

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Comments:

The available almond and pecan field trial data indicate that residues of diflubenzuron and metabolites CPU and PCA were each less than the method LOQ (<0.05 ppm for diflubenzuron and <0.005 ppm for CPU and PCA) in/on almond and pecan nutmeats harvested 27-28 days following the last of four foliar applications of the 25% WP, the 80% WDG, or the 2 lb/gal FIC formulation for a total seasonal application rate of ~1.5 lb ai/A/application (1.5x the maximum proposed seasonal rate for tree nuts); combined residues were <0.060 ppm in/on nutmeats. In almond hulls, residues ranged 0.972-5.532 ppm for diflubenzuron, <0.010 ppm (LOQ) for CPU, and <0.005 (LOQ)-0.0083 ppm for PCA in/on almond hulls; combined residues were <0.987-<5.547 ppm. The mean residues are <0.060 ppm for nutmeats and 2.542 ppm for almond hulls.

Almond and pecan samples from the submitted field trials were stored frozen for up to 5, 10.5, and 6 months prior to analysis for residues of diflubenzuron, CPU, and PCA, respectively. Adequate storage stability data are available to support the storage conditions and intervals of samples from this study.

Adequate sample chromatograms were provided.

Almond hulls are considered a significant feed commodity. The percent of almond hulls in dairy and beef cattle diets is 10% (90% DM).

III. CONCLUSIONS

Supervised crop field trial studies (MRIDs 45252209 and 45252210) in almonds conducted in CA (5 trials) and pecans conducted in GA (2 trials), LA (1), NM (1), and OK (1). Samples of almond and pecan nutmeats and hulls were collected 27-28 days following the last of four foliar applications of diflubenzuron at 0.5 lb ai/A/application (applications 1 and 4) and 0.25 lb ai/A/application (applications 2 and 3) for a total seasonal application rate of ~1.5 lb ai/A (1.5x the maximum proposed seasonal rate for tree nuts). For the almond field trials, side-by-side trials were conducted at one field site using the 25% WP formulation, the 2 lb/gal FIC formulation, and the 80% WDG formulation; the 25% WP formulation alone was used at the remaining field sites. For the pecan field trials, side-by-side trials using all three formulations were conducted at one GA site and the LA and OK sites, and the 2 lb/gal FIC formulation alone was used at the remaining GA site and the NM site. Combined residues of diflubenzuron and its metabolites CPU and PCA were less than the combined method LOQs (<0.060 ppm) in/on almond and pecan nutmeats and <0.987-<5.547 in/on almond hulls.

With respect to the side-by-side trials conducted in almonds and pecans, no significant differences were observed in residue levels in almond or pecan hulls following treatment with the 25% WP, the 80% WDG, or the 2 lb/gal FIC formulation in the side-by-side trials. Residues were <2.883 and <3.651 ppm, <3.409 and <5.547 ppm, and <2.921 and <3.140 ppm, respectively, in/on almond hulls following treatment with the 25% WP, the 80% WDG, and the 2 lb/gal FIC formulations. Residues were <0.080-0.771 ppm (n=6), <0.065-<0.381 ppm (n = 6), and <0.113-<1.392 ppm (n = 10), respectively, in/on pecan hulls (discussed here for informational purposes only) following treatment with the 25% WP, the 80% WDG, and the 2 lb/gal FIC formulations.

Based on the available method validation and concurrent recovery data, the analytical methods (HPLC for diflubenzuron and CPU, and GC for PCA) used to quantitate residues of diflubenzuron, CPU, and

Chemical Name Diflubenzuron
PC Code: 108201
EPA Barcode: D277691

Crop Field Trials
GL: OPPTS 860.1500
PP#1F06235

MRID: 45252209, 45252210
Case No.: 293515
Submission: S602900

PCA are adequate for data collection in/on almond and pecan nutmeats and hulls. The validated method LOQs were <0.05 ppm for diflubenzuron in/on nutmeats and hulls, <0.005 and <0.010 ppm for CPU in/on nutmeats and hulls, respectively, and <0.005 ppm for PCA in/on nutmeats and hulls. No interference was observed in representative chromatograms of control samples from the analysis of almond and pecan nutmeats and hulls.

The trials were conducted at 1.5x the maximum proposed application rate. However, the final application of the test substance (typically the application that determines the residues in the crop at harvest) was made at the maximum per application rate. Because the *per application rate was 1x*, the crop field trials for tree nuts are classified as acceptable. The data satisfy the guideline requirement for crop field trials (Residue Chemistry Guidelines OPPTS 860.1500) for tree nuts. Based on the results of these trials, the petitioner should propose a tolerance of 6.0 ppm for the combined residues of diflubenzuron, CPU, and PCA in/on "almond, hulls."

IV. STUDY DEFICIENCIES

No deficiencies were identified.

V. REFERENCES

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From: J. Rowell
To: D. Marlow
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Chemical Name	Diflubenzuron	Crop Field Trials	MRID: 45252209, 45252210
PC Code:	108201	GL: OPPTS 860.1500	Case No.: 293515
EPA Barcode:	D277691	PP#1F06235	Submission: S602900

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To: M. Johnson/A. Sibold
Date: 2/17/99
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Date: 5/31/01
MRIDs: None

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To: H. Jamerson
Date: 9/20/01
MRIDs: None



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Chemical: Diflubenzuron

PC Code: 108201

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